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National Bureau of Standards

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MATHEMATICAL TABLES

A list of the mathematical tables now obtainable from the National Bureau of Standards is printed on pages 3 and 4 of the JOURNAL cover. New tables will be announced from time to time as they become available.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1563

Part of Journal of Research of the National Bureau of Standards, Volume 31, November 1943

ABRASION AND SOLUTION OF TEETH

By Wilmer Souder and Irl C. Schoonover

ABSTRACT

Minute changes in the surfaces of teeth are detected by observing the injury to calibrated indentation marks made in these surfaces by a diamond hardness indenter.

Abrasive and chemical injuries are disclosed by observing or photographing a series of these marks, so placed that each small area is definitely identifiable.

Objectionable abrasives in dentifrices are readily detected by brushing a tooth surface on which indentations have been placed.

The indentations also give an indication of the hardness of the tooth and enable the investigator to select areas of known hardness for experimental tests.

Some data are presented to show the initial effects of chemical solutions and bacterial actions, which may play important roles in the development of dental caries.

Eleven figures and two tables correlate the experimental work.

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I. INTRODUCTION

Evaluations of experimental data on abrasion or solution by dentifrice or by the causes responsible for dental caries are usually accompanied by difficulties and uncertainties. These arise from such unknown factors as:

(a) How hard was the tooth tested?

(b) How much of the effect was on enamel, and how much was on other constituents of the tooth?

(c) Did the tooth absorb or lose water during the test or weighings?

(d) Is the abrasiveness of a dentifrice, rubbed or brushed against a metallic or vitreous surface, comparable to its abrasiveness when brushed against a tooth?

The Bureau was called upon during the year 1942 to make an investigation of certain brands of dentifrice for an agency of the United States Government. During the investigation it was necessary to devise a method that would make it possible to follow more precisely and more intelligently the changes taking place during the use of a dentifrice. In other words, it was necessary to find whether a change in weight of a brushed tooth resulted from: a loss or a gain in water content, changes in composition, abrasion, solubility of tooth structures, or some combination of these possible causes.

It seemed sound, experimentally, to employ one of the marking or scratching methods used to determine the wear of bearing surfaces to secure visual evidence of the progress of injury to teeth. Any instrument capable of placing, repeatedly, small marks of known dimensions in enamel or dentin surfaces may be used, provided losses of surface layers or changes in surface structures are revealed by proportionate changes in these marks.

The Knoop pyramidal-diamond indenter,[1] when pressed into flat surfaces, under a constant load, produces indentations of definite depth, width, and length (see fig. 1). It served well in this research. These depressions in the surface are clearly outlined and easily photographed.

Surfaces of enamel or dentin so marked and photographed may then be exposed to the action of an abrasive, a chemical, or a dentifrice and again photographed, after the exposure (see fig. 2). The changes will be evident when the photographs are compared. From such comparisons it is possible to establish on a single tooth the damage to enamel or dentin developed during the experimental procedure. This is a definite advantage not inherent in many other methods employed for studying these problems.

II. EXPERIMENTAL DATA

The following experimental data and figures were obtained, using this method to investigate the attack by the materials indicated on the enamel and dentinal surfaces of teeth.

The linear magnifications of the figures shown in this report are, for figures 1, 4, and 5, B, equal to ×135, and for the remainder, equal to ×45 when printed to a width of 2⅜ inches. Where the surface contains dentin, the dentin is on the lower-right area of the figure.

1. ABRASION OR SOLUTION PRODUCED BY DENTIFRICES

The problem was to determine whether the observed weight losses of teeth brushed with the two dentifrices in question resulted from abrasion or solution of the tooth structure.

The brushing tests were made on the enamel and dentin surfaces of crown sections of teeth cut off above the pulpal chamber. They were held against a rotating bristle wheel with a load just below that necessary to stall the wheel. The teeth were interchanged, so that in most instances each tooth was tested with the three dentifrices. Data for these tests are reported in table 1. (An approximate evaluation of the brushing effect of the rotating brush in terms of hand-brushing gives 3 minutes of the rotating brush equal to 1 year of normal or average hand-brushing.) Definite injury was produced by hand-brushing, using both dentifrices (*A* and *B*), as shown in figures 4 and 5.

[1] Frederick Knoop, Chauncey G. Peters, and Walter B. Emerson, *A sensitive pyramidal-diamond tool for indentation measurements*, J. Research NBS **23**, 39 (1939) RP1220.

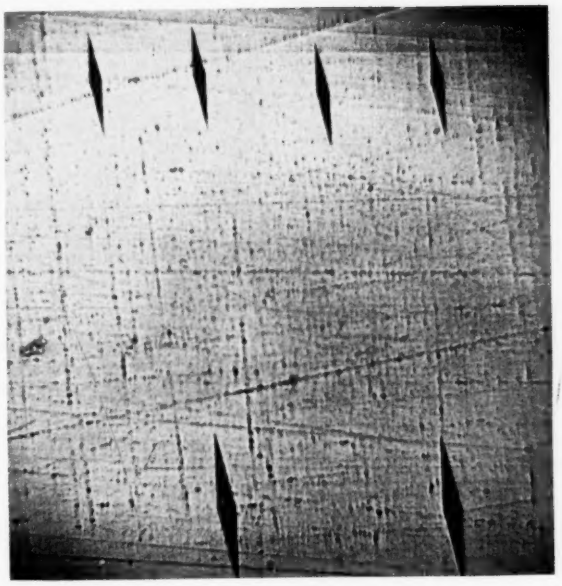

FIGURE 1.—*Dental enamel surface polished and indented.*
In figures 1, 4, and 5, the longer indentations are the result of heavier loads.

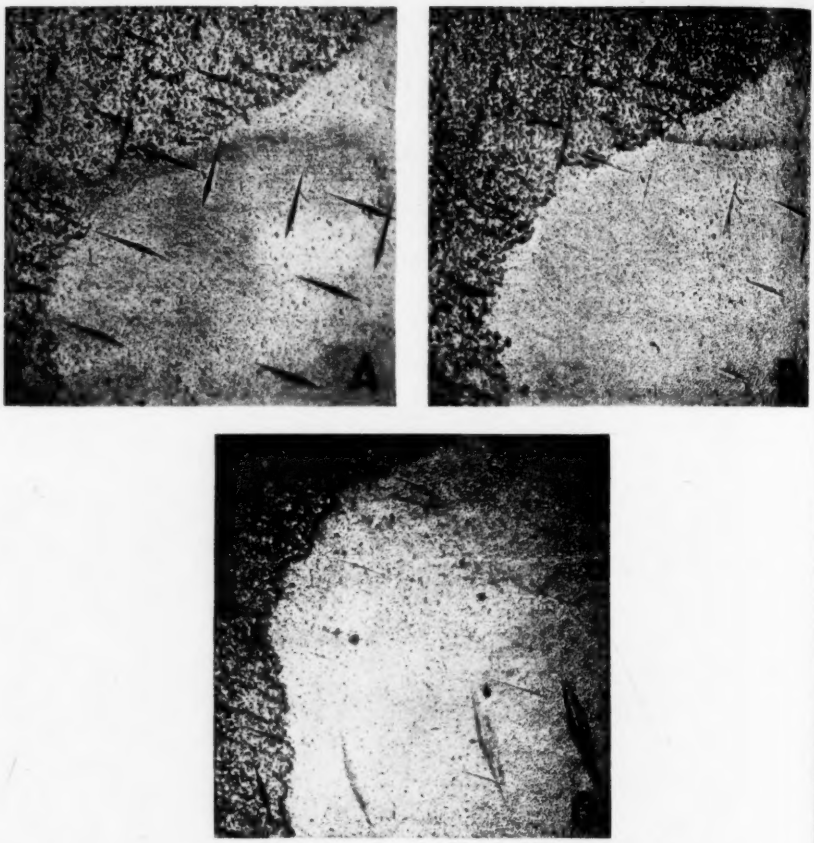

FIGURE 2.—*Enamel-dentin surface polished and indented.*

A, original surfaces; *B*, same surface after 5 days' exposure to a water solution of powder *A*; *C*, same surface after 4 months' exposure to the water solution of powder *A*. The diamond hardness indenter was again applied to the surface (at the end of the 4 months) with the same load as that used on *A*. The solvent and softening actions are evident.

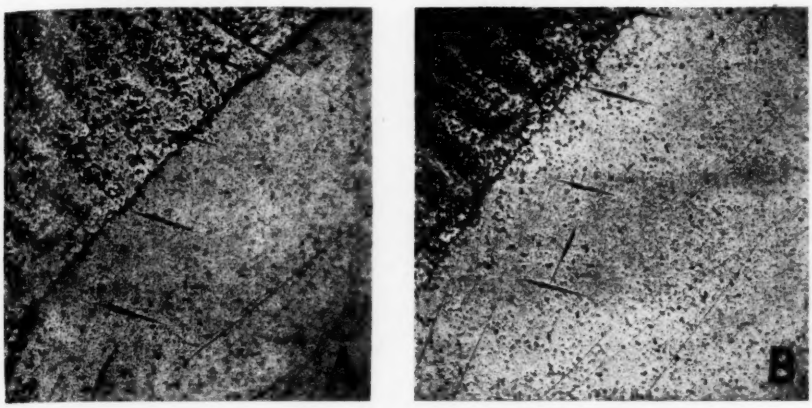

FIGURE 3.—*Enamel-dentin surfaces polished and indented.*

A, original surfaces; *B*, same surfaces after 5 days' exposure to a water solution of powder *B*. No solvent action on the dentin is evident.

FIGURE 4.—*Dental enamel surface polished, indented and brushed 25 minutes by hand with a waterpaste of powder A.*

Note the difference between an apparent solvent action here and the abrasive action so evident in figure 5.

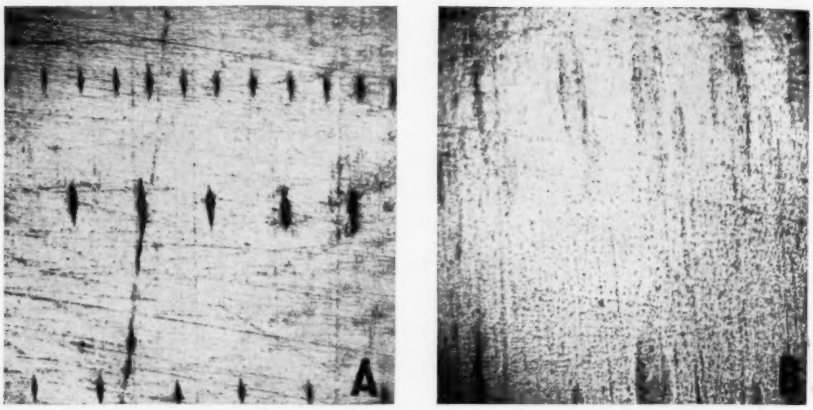

FIGURE 5.—*Dental enamel surfaces polished and indented.*

A, same area as figure 1, brushed 25 minutes with powder *B*; *B*, same area as figure 4, brushed 25 minutes with powder *B* after 25 minutes of brushing with powder *A*.

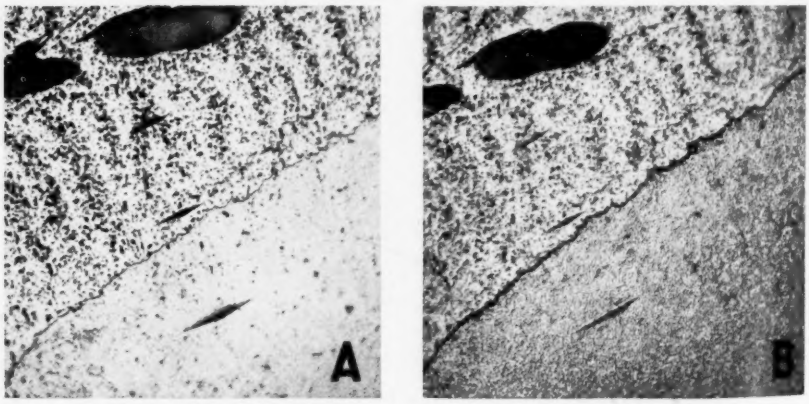

FIGURE 6.—*Enamel-dentin surfaces polished and indented.*

A, original surfaces; *B*, same surfaces after 4 days in a 20-percent solution of granulated sugar in water. (The darker ovals are folds where the contour of the enamel runs below the plane of polish.)

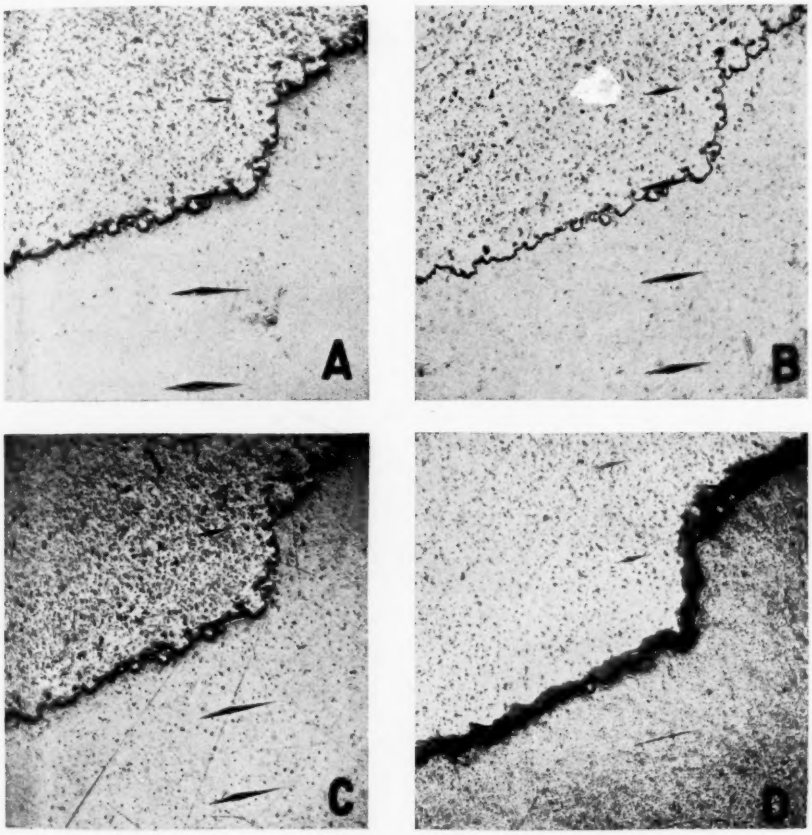

FIGURE 7.—*Enamel-dentin surfaces polished and indented.*

A, original surfaces; *B*, same surfaces after 5 days in water solution—sugar and calcium hydroxide (20 g of sugar and 5 g of $Ca(OH)_2$ per 100 ml of water); *C*, same surface after 6 days in a sterile 20-percent sugar solution; *D*, after 6 days in a 20-percent sugar solution, to which had been added 20 g of $CaSO_4$ and 2 ml of saliva for each 100 ml of solution.

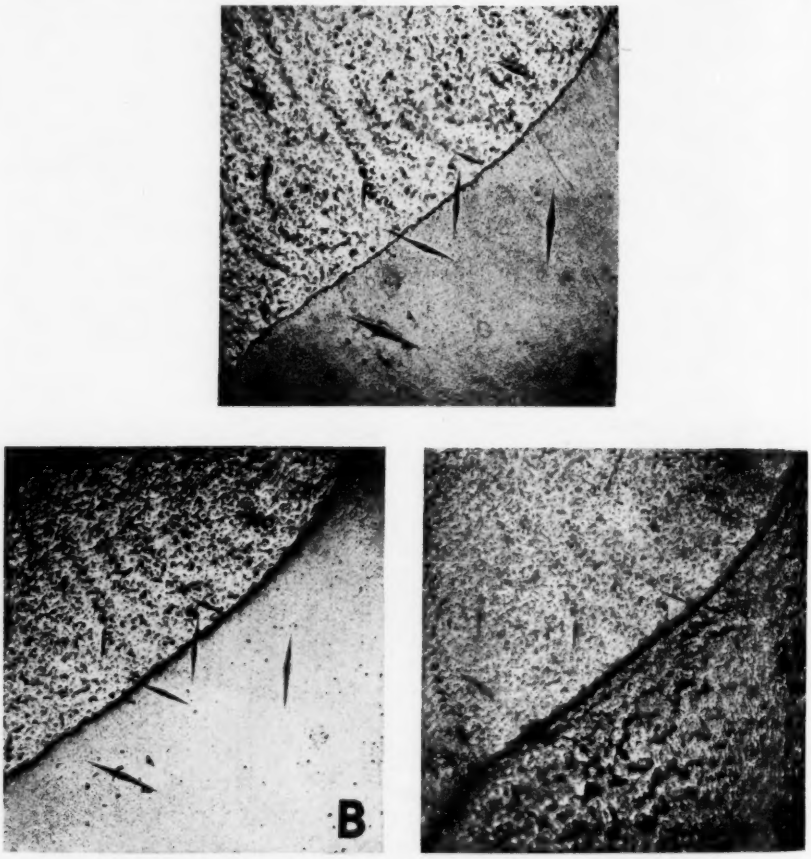

FIGURE 8.—*Enamel-denlin surfaces polished and indented.*

A, original surfaces; *B*, after 5 days in a crude molasses (pH 4.3); *C*, after 5 days in a solution containing 20 g of granulated sugar and 2 g of sodium alginate per 100 ml of water (pH 4.3).

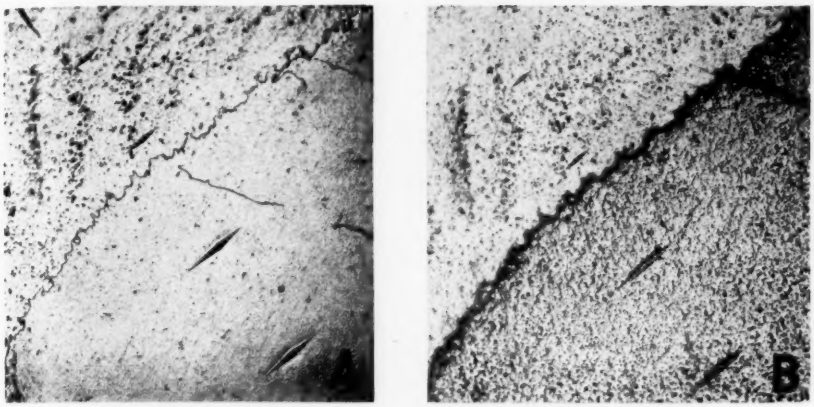

FIGURE 9.—*Enamel-dentin surfaces polished and indented.*

A, newly polished surfaces; *B*, same surfaces after 5 days in a "raw" sugar solution (pH 4.0).

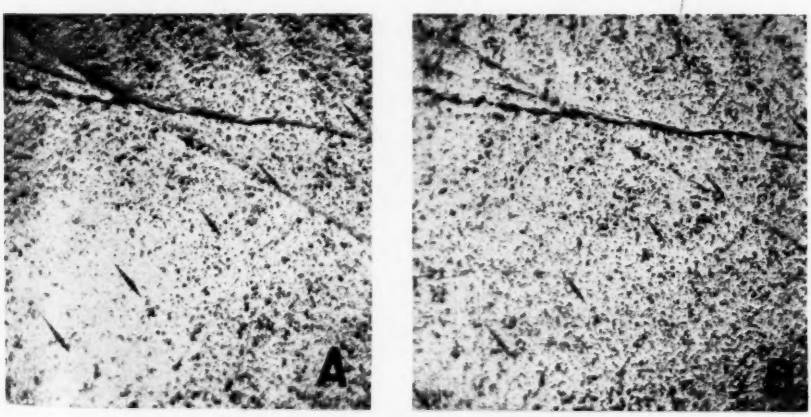

FIGURE 10.—*Dental enamel polished and indented.*

A, white spot in enamel surrounded by clearer enamel; *B*, the same area after 5 days in a "raw" sugar solution.

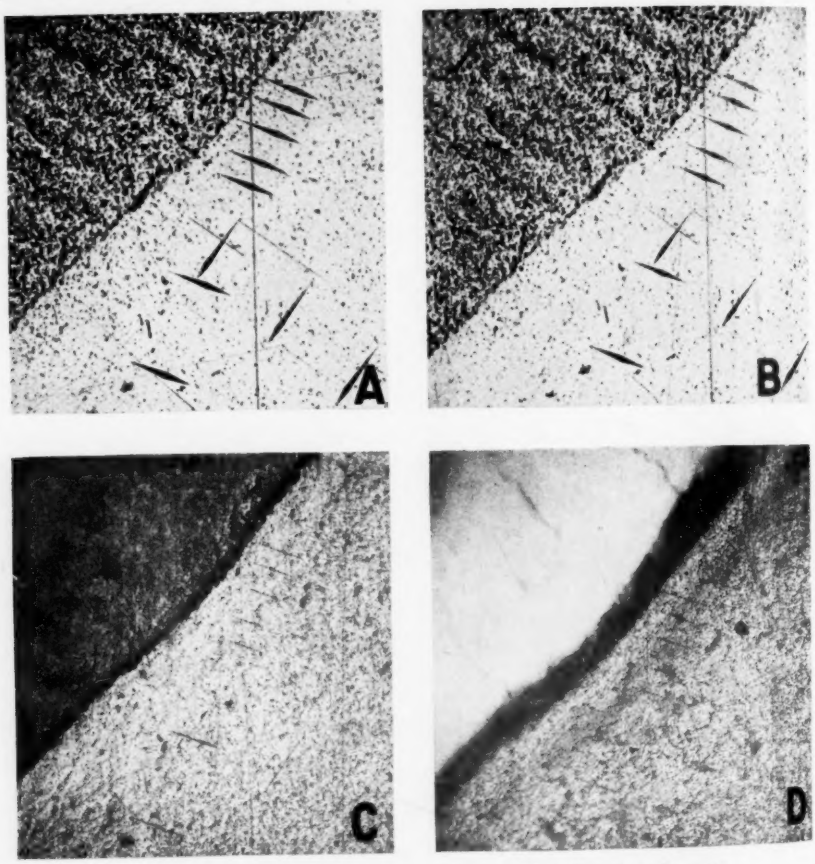

FIGURE 11.—*Enamel-dentin surfaces polished and indented.*

A, polished surfaces; *B*, after 9 days in a water mixture containing a base exchange material; *C*, after 24 hours in a diluted hydrofluoric acid solution; *D*, after 9 days in a sugar solution containing mouth bacteria.

TABLE 1.—*Losses of enamel and dentin during brushing*

[Wheel brush, ⅝-inch, driven at 1,750 rpm]

Brushing agent	Loss in weight [a]
Dental enamel (duration of tests 25 min)	
	mg
Powder *A*	1.1
Powder *B*	1.3
Paste *C*	1.0
Powder *A* plus 25% of FF carborundum	15.6
Water	0.0
Dentin (duration of tests 3 min, average)	
Powder *A*	22.6
Powder *B*	34.6
Paste *C*	7.0
Water	[b] +0.2

[a] Average for 2 or more tests.
[b] Apparent gain only. Accuracy of weighings is thought to be ±0.2 mg.

The principal solid ingredient of powder *A* is said to be sodium metaphosphate, plus a minor percentage of tricalcium phosphate. It is known to be soft, and is claimed to be insoluble. In fact the powder showed no abrasive scratches when rubbed against glass and is said to show little abrasion when rubbed against metal. The loss of enamel during brushing with a ⅝-inch dental wheel driven at 1,750 revolutions per minute and constantly bathed in a water-powder mixture was approximately the same as the loss produced by powder *B*, known to contain abrasives. These losses of enamel are small and perhaps are of minor dental significance (see table 1). The loss of dentin for soft powder *A* is, however, three times as much as the loss for paste *C*, a dentifrice which complies with a Federal specification.[2]

The question naturally arises: How can a slightly abrasive dentifrice do so much damage to the dentin of a tooth? A suspicion that solvent action was occurring arose when the surface injury shown in figure 4 was examined. This surface did not reveal typical abrasive injury. The injury produced when powder *B* was brushed by hand, precisely as powder *A* was brushed, against another surface of enamel showed typical abrasive injury (see fig. 5, A.) The surface, in figure 5, B, near the identations appeared to have been scooped out and pushed away. The surface brushed with powder *A* did not show this uniform removal of enamel over the entire brushed area. There appeared to be local pitting, or honeycombing, of the surface and the general outline of the indentation was better preserved, although there were typical edge and angle losses on the indentation, which are characteristic of chemical attack. This was confirmed in the following tests.

Plane surfaces were cut on teeth selected for the maximum of apparent soundness. The cutting to plane surfaces was done progressively on flat disks, using finer and finer carborundum powder as the cutting agent. The final polish was produced on a velvet-coated

[2] Federal Specification for Dentifrice; Tooth paste, FFF-D-191a.

disk, using wet magnesium oxide as the polishing agent. Marks were placed on both the enamel and dentin surfaces with the indenter, and the teeth were immersed in a mixture of water and the dentifrice to be tested.

The chemical attack on the exposed dentin shown in figure 2, B, developed from the wet dentifrice powder *A* applied to the tooth for 5 days without any brushing. The test was repeated on other teeth with the same result. After 4 months, the hardness indenter was again pressed into the surface of the tooth shown in figure 2, A, (see fig. 2, C) with the same load as that used for the specimen in figure 2, *A*. The dentin had been softened, as is evident from the greater penetration of the diamond indenter. The original normal hardness of about 50 (Knoop number) dropped to about 20 for the surface of the dentin. Figure 3, B, shows no such effect when a tooth is similarly treated with another wet dentifrice, powder *B*. Hardness tests on the surface shown in figures 3, A, and 3, B, were repeated at the end of 5 months' exposure to powder *B*. No such attack as that disclosed in figure 2, B, or 2, C, was evident. The fine scratches left in polishing the tooth were still visible after the 5 months' exposure. Dentifrice powder *A* mixed with water chemically attacks tooth surfaces.

Further confirmation of chemical attack was obtained in the following experiments. Small sections, such as cusps, were cut from teeth and were conditioned by storage in water for a number of days. They were then washed in alcohol and ether for quick drying and weighed on a magnetically damped balance. After the weighing, they were stored for 20 days in solutions of dentifrices *A*, *B*, and *C*. Powder *A* caused losses in weight of 0.2 percent and established the solvent action by the dentifrice. See table 2. This is not surprising, as sodium metaphosphate is a chemical frequently recommended to produce decalcification, when such action is desired in industry. Dentifrice *A* yielded 0.3 percent soluble phosphate rather consistently, even after 15 leachings. Figure 2 confirms the damage indicated in table 2. Perhaps the greatest injury to be anticipated from dentifrices containing such decalcifying ingredients would come from the particles of powder lodged between the teeth or under the gums, where they may be expected to continue their action during 24 hours of each day, unless they are completely dissolved before the next application of dentifrice.

TABLE 2.—*Solvent action of two tooth powders*

[Sections of teeth immersed in diluted dentifrice]

Initial weight of tooth crown	Weight after 20 days	Loss in weight
Powder *A* in water (saturated solution)		
mg	*mg*	*mg*
605.3	604.3	1.0
510.2	509.0	1.2
841.8	840.0	1.8
228.0	227.3	0.7
Powder *B* in water (saturated solution)		
677.2	677.1	0.1
381.9	382.0	*.1
285.2	285.2	.0
Distilled water		
436.3	436.1	0.2
146.9	147.0	*.1

* On these specimens there was an apparent gain. Since the accuracy of the weighings is thought to be ±0.2 mg, a gain in weight is not established.

2. ATTACK BY OTHER CHEMICALS AND BY BACTERIA

This method of investigation has also been used in a preliminary study of the effects of materials other than commercial dentifrices, such as sugar solutions, fluorides, alginate (a recent component in some dentifrices), and similar chemicals, in the hope that data of value in researches on dental caries might be obtained. It has not been possible to complete these studies. The following figures and comments are recorded, with little attempt therefore to evaluate their significance.

Figures 6 to 11, inclusive, show the effect of exposing tooth enamel and dentin to sugar solutions under various conditions. One of the theories of dental caries is based on the idea that refined sugars, when acted upon by various oral organisms, produce organic acids that attack tooth surfaces. If this process is confined in an isolated and protected area, carious lesions are said to result from such acid attack.

Figure 6 shows: A, the freshly polished surfaces of enamel and dentin; and B, the same surfaces after 4 days in a 20-percent solution of granulated sugar. No attempt was made to sterilize the sugar solution or to prevent bacterial action. Definite attack of the tooth surfaces is evident from the lack of sharp and definite edges of the indentation marks in figure 6,B. The darker ovals in the enamel are folds where the contour of the enamel runs below the plane of polish.

Figure 7 shows: A, the polished surface of enamel and dentin treated in sequence; B, 5 days in a water mixture containing 20 g of granulated sugar and 5 g of calcium hydroxide, $Ca(OH)_2$, for each 100 ml of water (the pH of this solution was 12.3); C, the same surface after 6 days in a sterile water solution containing 20 g of granulated sugar for each 100 ml of water (the pH of this solution was 6.7), and D, after 6 days in a

water mixture containing 20 g of granulated sugar, 20 g of calcium sulfate, and 2 ml of fresh saliva for each 100 ml of water (the pH of this solution after 6 days was 3.3). No attack was observed in the sugar solution rendered alkaline by the calcium hydroxide, nor was there any attack by the sterile sugar solution in which bacterial action was prevented. Severe attack did occur, however, when bacterial action was permitted in the sugar solution containing the calcium sulfate. (In this and the following experiments in which bacterial action is discussed, actual bacteria counts were not made. Bacterial action was assumed to have occurred when gas bubbles could be observed escaping from the solution and when the solutions became progressively more acid.)

Figure 8 shows: A, newly polished surfaces of enamel and dentin; B, after 5 days in a crude, not sterilized, molasses (pH 4.3); and C, after 5 days in a water solution containing 20 g of granulated sugar and 2 g of sodium alginate for each 100 ml of water. The pH of this solution at the time the tooth was immersed was 4.3. It is of interest to note that no attack of the tooth surfaces occurred in the crude molasses, and that the same surfaces were severely attacked by the refined sugar solution.

Figure 9 shows: A, newly polished surfaces of enamel and dentin, and B, after 5 days in a water solution containing 20 g of raw sugar for each 100 ml of water. (The pH of this solution was 4.0.) Severe attack occurred. It should be pointed out that although the raw sugar is a crude product, some refining has been done, and it is not as crude as the molasses used in the previous experiment.

Figure 10 shows: A, a white spot in the enamel surrounded by clearer enamel, and B, the same surface after 5 days in a water solution containing 20 g of raw sugar for each 100 ml of water. The white area was definitely softer than the surrounding clear enamel as is indicated by the longer marks in the white area. The actual Knoop hardness numbers were around 250 (kg/mm^2) for the white area, and numbers up to 350 were obtained for the clear enamel. Such soft white areas are considered by some dentists to be more susceptible to attack, and are the areas where carious lesions are most likely to occur, provided the white spot extends to the surface of the tooth.

Figure 11 shows: A, newly polished surfaces of enamel and dentin; and B, after 9 days in a mixture containing 100 g of a base exchange material (1R4 sold by Resinous Products Chemical Co., Philadelphia, Pa.) to each 100 ml of water; C, after 24 hours in diluted solution of hydrofluoric acid (approximately 1 part per million); and D, after 9 days in a water solution containing 20 g of granulated sugar and 2 ml of fresh saliva for each 100 ml of water. It is evident that the hydrofluoric acid solution was too concentrated. The fluoride treatment, however, afforded no protection to the tooth against further attack by the sugar saliva solution, as shown in figure 11,D, in which the enamel is severely corroded.

Sections of the teeth stored in sugar solutions for several months (minimum about 2 months), in which bacterial action was not prevented showed severe attack on the enamel and much less attack on the dentin. Actually, the enamel could be pushed away as a sort of paste-like coating, leaving the dentin sacrcely attacked at all below the orinigal surface. The same general type of attack is illustrated by the enamel in figure 11,D, after storage for 9 days in a sugar solution.

III. SUMMARY

A method of research more searching in its application and permitting more definite visualization of injury to teeth than hitherto used is described.

The injury to enamel from a dentifrice containing harsh abrasives is definitely evident after 25 minutes of brushing with a toothbrush using a technique similar to that employed daily by millions.

The injury to enamel and dentin from a dentifrice containing a decalcifying ingredient is shown.

A few surfaces of enamel and dentin have been photographed before and after exposure to conditious thought to initiate or to foster dental caries.

This method of investigation offers exceptional opportunities for studying minute areas of teeth, enamel-dentin, and tooth-restoration margins with a definiteness not hitherto available. It should be of unusual value in laboratory studies of dental caries, where it will be possible to detect in a few days changes in tooth structures that might require weeks or months by other methods.

WASHINGTON, August 2, 1943.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1564

Part of Journal of Research of the National Bureau of Standards, Volume 31, November 1943

REPORT ON THE SYSTEMS LEAD OXIDE–ALUMINA AND LEAD OXIDE–ALUMINA–SILICA

By R. F. Geller and E. N. Bunting

ABSTRACT

Phase relations were studied for those portions of the binary and the ternary systems containing over 50 percent of PbO. It is reasonably certain that the binary system contains the compound $PbO.Al_2O_3$. In the ternary system 3 compounds ($8PbO.Al_2O_3.4SiO_2$, $4PbO.Al_2O_3.2SiO_2$, and $6PbO.Al_2O_3.6SiO_2$) were identified, 4 others were indicated by optical and X-ray properties, and 10 quintuple points, which include 6 eutectics, were established. Also, Al_2O_3 (99.9 plus purity) was observed to melt at 2,035 °C.

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I. INTRODUCTION

This report is published in order that the limited information given may be available for use now rather than to wait until more peaceful times make it possible to complete the study.

Because of extremely slow crystallization rates and other unfavorable characteristics of compositions over the greater portion of these two systems, the progress of the work has been very slow. Three years were required to obtain the data presented at this time, and there is every indication that experimental difficulties will increase as the explored area is extended toward the $Al_2O_3-SiO_2$ side of the diagram. The study is a part of the broad survey of systems containing PbO that has been in progress since 1932.[1]

The $PbO-SiO_2$ system (see footnote 1) and the system $Al_2O_3-SiO_2$[2]

[1] R. F. Geller, A. S. Creamer, and E. N. Bunting, J. Research NBS **13**, 237 (1934) RP705; R. F. Geller and E. N. Bunting, J. Research NBS **17**, 277 (1936) RP911; **18**, 585 (1937) RP995; **23**, 275 (1939) RP1231.
[2] N. L. Bowen and J. W. Greig, J. Am. Ceram. Soc. **7**, 238 (1924); J. Wash. Acad. Sci. **14**, 183 (1924).

have been investigated. A limited study of the reaction $PbO \rightleftarrows Pb_3O_4$ was made in connection with this investigation, and the report was published recently.[3]

II. EXPERIMENTAL PROCEDURE

1. MATERIALS

For compositions prepared directly by fusion, the end members were (a) sublimed litharge containing 0.02 percent of total detected impurities; (b) Al_2O_3 prepared by converting aluminum metal of 99.95 percent purity to the nitrate and heating at 1,200° C to form the Al_2O_3; and (c) pulverized quartz containing 0.02 percent of nonvolatile residue on evaporation with HF and H_2SO_4.

After fusion in platinum, using an electrically heated furnace, the various melts were analyzed chemically (by A. S. Creamer).

When it was necessary to heat specimens at temperatures in excess of about 950° C, the volatilization of PbO became noticeable, and this tendency increased with decrease in the SiO_2 content. To avoid the excessive volatilization of PbO during the preparation of melts containing little or no SiO_2, a number of compositions were made by coprecipitation prior to fusion, of a nitric acid solution of the litharge already described and reagent quality $Al(NO_3)_3.9H_2O$ in the presence of silica gel of 99.96 percent purity.

For the determination of the melting point of Al_2O_3, a sample of the oxide was prepared by dissolving aluminum metal of over 99.98 percent purity[4] with reagent quality HNO_3 and igniting at 1,100° C. All reactions were carried out in platinum.

2. TEST METHODS

Thermal studies were made by the usual quenching method, using precrystallized samples, of which portions were heated at successively higher temperatures until liquidus was obtained. The specimens for crystallization and for quenching were contained in platinum foil, and it was customary to hold the specimen at least overnight before each quench. The quenching studies were supplemented, in a few cases, with heating curves by the differential thermocouple method. All heatings were made in electrically heated furnaces, and the Pt to Pt-Rh thermocouples were calibrated by observing the melting temperature of KCl (770.3° C) and K_2SO_4 (1,069.1° C). Unless otherwise noted in the text or the tables, critical temperatures may be considered accurate to ±2° C.

Compositions containing over about 90 percent of PbO could be crystallized by holding at a suitable temperature for several hours, but this holding time increased greatly with decrease in PbO content. For melts containing 50 to 60 percent of PbO, for example, it was not unusual to develop only partial crystallization after treatments of from 1 to 2 months' duration.

Examination of treated specimens with the petrographic microscope was made in all cases. The results were verified, when necessary, with X-ray diffraction patterns made and interpreted by H. F. McMurdie. Details of these examination methods have been described.[5]

[3] NBS Tech. News Bul. 315, p. 52 (July 1943).

[4] Furnished by James I. Hoffman, and described by him and G. E. F. Lundell in J. Research NBS 18, (1937) RP957.

[5] R. F. Geller and E. N. Bunting, J. Research NBS 23, 278 (1939) RP1231.

The Al_2O_3 melting point was observed with an optical pyrometer while the specimen was resting on an iridium pedestal in an electrically heated furnace.[6] The pyrometer calibration was certified to ±10° C by the Pyrometry Section of this Bureau.

III. THE SYSTEM PbO-Al_2O_3

The existence of a eutectic at about 865° C and 94 percent of PbO between PbO and a compound of PbO and Al_2O_3 seems reasonably certain (fig. 1) and the data suggest the compound $PbO.Al_2O_3$ for two reasons: (a) the absence of a break in the heating curve of the compound composition at about 865° C. This break occurred con-

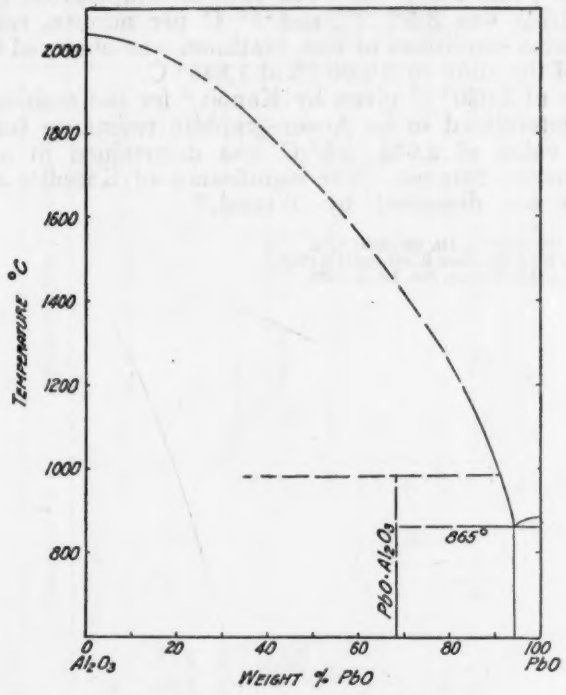

FIGURE 1.—*The system* PbO-Al_2O_3

sistently for the compositions higher in PbO than the 1:1 ratio and is believed to show the $PbO.Al_2O_3$-PbO eutectic temperature (table 1); and (b) the most nearly complete crystallization to one phase was obtained with the PbO and Al_2O_3 in equimolar ratio (table 1). Beyond this composition, in the region of higher Al_2O_3 content, the true phase relations are largely conjectural, and were not investigated further because of the extremely rapid volatilization of PbO during both the preparation of melts and the crystallization trials.

The phase assumed to be $PbO.Al_2O_3$ [7] is uniaxial negative, has indices of refraction ϵ1.85, ω1.91, crystallizes in platy form, and the diffraction data are given in table 2. The data summarized in table 1

[6] R. F. Geller, J. Research NBS 27, 555 (1941) RP1443.

[7] When references are made in this report to the compound $PbO.Al_2O_3$, it should be remembered that its existence has not been definitely established.

indicate that it breaks down rapidly at about 1,000° C to form beta Al_2O_3 and liquid. Whether this "break down" is a true incongruent melting, or a decomposition accelerated at 970° to 1,000° C and resulting from volatilization of PbO, is not clear. The latter explanation seems plausible in view of the heating-curve results on melt 5, which showed a drift, beginning at about 970° C, rather than a definite break.

Solid solution in this system is indicated. In some melts the indices of refraction of the $PbO.Al_2O_3$ varied, being slightly lower. Also, in some cases the alpha alumina had indices of refraction above 1.765 probably because of PbO dissolved in the crystal.

The Al_2O_3 sample was observed, in three tests, to melt sharply at 2,040°, 2,030°, and 2,030° C. The rate of temperature rise at the time of melting was 3.5°, 2°, and 5° C per minute, respectively. Under the same conditions of test, platinum was observed to melt at 1,770° C and the alloy 10 Rh-90 Pt at 1,845° C.

The value of 2,050° C given by Kanolt [8] for the melting point of Al_2O_3 was determined in an Arsem-graphite resistance furnace, and Bunting's [9] value of 2,045 ±5° C was determined in a high-frequency induction furnace. The significance of Kanolt's and Bunting's values are discussed by Wensel.[10]

[8] C. W. Kanolt, BS Sci. Pap. **10**, 295 (1914) S212.
[9] E. N. Bunting, BS J. Research **6**, 947 (1931) RP317.
[10] H. T. Wensel, J. Am. Ceram. Soc. **19**, 81 (1936).

TABLE 1.—*Quenching tests, heating-curve results, and X-ray examinations for the PbO-Al*

TABLE 1.—*Quenching tests, heating-curve results, and X-ray examinations for the* PbO-Al_2O_3 *system*

Melt No.	Composition: Approximate mole ratio PbO	Composition: Approximate mole ratio Al_2O_3	Composition: By weight PbO	Composition: By weight Al_2O_3	Heating curve breaks	Quenching tests: Heat treatment			Quenching tests: Crystalline phases produced [a]	Crystalline phases found by X-ray examination
						Days	hr	°C		
			%	%	°C					
15 [b]			[c] 97.0	[c] 3.0	865, 869					
1			[c] 95.0	[c] 5.0	864	6		[c] 700	PbO, and uniaxial negative crystals of η1.84 to 1.87.	
14 [b]			94.9	5.0	865, 868					
13 [b]			93.0	7.0	864, 951					
11 [b]			92.0	8.0	864, 951					
9 [b]			91.5	8.5	864, 957					
2			[c] 90.0	[c] 10.0		6		[c] 700	Same as melt 1	
			[c] 90.0	[c] 10.0			1.5	1,100	do	
			[c] 90.0	[c] 10.0			1.5	1,350	Mostly Al_2O_3, also crystals of η1.84 to 1.87	
3 [b]	2	1	81.9	18.1	865	14		800	Crystals having η1.85 to 1.91	Same as melt 5 (800°).
4 [b]	3	2	76.9	23.1	864	13		800	do	
5 [b]	1	1	68.6	31.4	(d)	15		800	About 80 percent crystals of η1.85 to 1.91	Phase assumed to be $PbO.Al_2O_3$ (pattern, table 2).
	1	1	68.6	31.4			1	900		βPbO.[e]
	1	1	68.6	31.4			1	1,000		Same as melt 5 (800°).
	1	1	68.6	31.4			1	1,150		αPbO and βAl_2O_3 (?).
	1	1	68.6	31.4			½	1,200		Do.
	1	1	68.6	31.4			½	[f] 1,200		βAl_2O_3 (?).
	1	1	68.6	31.4			¼	1,250		αPbO and βAl_2O_3 (?).
10	1	1	[c] 68.8	[c] 31.2		6		700	Some crystals identified as uniaxial negative η1.84 to 1.87.	
	1	1	[c] 68.8	[c] 31.2			20	1,200	Al_2O_3 and possibly Al_2O_3 with PbO in solution	
7	3	4	61.8	38.2	970	18		800	About 33% crystals having η1.85 to 1.91	
6	2	3	59.2	40.8	1,010	14		800	About 25% crystals having η1.85 to 1.91	
8	1	2	51.2	47.8		11		800	do	Same as melt 5 (800°) plus a few unidentified lines.
	1	2	51.2	47.8			1	900		Same as melt 5 (800°).
	1	2	51.2	47.8			1	1,000		αPbO and βAl_2O_3 (?).
	1	2	51.2	47.8			1	1,200		Do.

[a] The melts heated above 1,000° attacked the Pt capsules and had crystallized in part on the outer surface. The portion remaining on the inside was usually darker in color and apparently higher in PbO content.

[b] Mixture prepared by coprecipitation.

[c] Not analyzed chemically. Percentages based on batch weights.

[d] Pronounced "drift" beginning at about 970° and indicating volatilization of PbO.

[e] Prefused in the capsule at 1,250° and then held as indicated.

[f] Platinum capsule left open.

[g] This heat treatment probably insufficient to develop the $PbO.Al_2O_3$.

TABLE 2.—*Diffraction data for the compound assumed to be* $PbO.Al_2O_3$ *(by H. F. McMurdie)*

[*VS*=very strong; *S*=strong; *M*=medium; *W*=weak; *VW*=very weak]

Estimated intensity	*d*	Estimated intensity	*d*
	A		*A*
M	4.66	*M*	1.963
S	4.43	*M*	1.916
W	4.22	*M*	1.897
M	4.05	*W*	1.776
VS	3.08	*M*	1.680
M	2.621	*VW*	1.637
M	2.507	*VW*	1.613
VW	2.367	*VW*	1.598
VW	2.303	*W*	1.576
S	2.221	*W*	1.540
W	2.165	*W*	1.519
VW	2.140	*VW*	1.508
W	2.097	*W*	1.471
VW	2.009	*W*	1.453

IV. THE SYSTEM PbO-Al_2O_3-SiO_2

Stability fields have been established with some approach to completeness in that portion of the system containing over 80 percent of PbO. The remainder of the diagram, as indicated in figure 2, is believed to be occupied largely by the fields of corundum and of mullite, with silica primary in a narrow strip extending along the PbO-SiO_2 border.

1. THE SILICA, MULLITE, AND CORUNDUM FIELDS

Silica field.—It was possible to establish that the silica field does not extend beyond 2 percent of Al_2O_3 for compositions containing from 30 to 35 percent of SiO_2. Tridymite is the primary phase in melt 158 (fig. 2 and table 3), but silica is not primary in melts 112, 130, and 143. It seems reasonable to assume that the compositions of the silica boundary are approximately on a straight line and extend, as indicated, from the established eutectic composition in the Al_2O_3-SiO_2 system to the quintuple point at the junction of the quartz-$PbO.SiO_2$ boundary with the adjoining ternary field. The liquidus temperature at this quintuple point, which is also a eutectic, is between 720° and 725° C, as evidenced by the quench results for melts 113 and 143 (table 3).

Mullite field.—The identification by X-ray pattern of mullite as the only crystalline phase in melt 201, heated at 1,450° C (table 3), establishes this compound as the primary phase for that composition. The same composition, heated at 880° C for 10 weeks, contained unidentified lath-like crystals having refractive indices 1.69 max and 1.67 min and another crystalline phase resembling mullite, but no lines for the latter were present in the X-ray pattern. Since mullite was not found in melts 128 and 204, the field probably ends approximately as indicated (fig. 2), and the boundary temperatures may be

expected to decrease toward the tridymite field. This assumption is supported by the fact that the liquidus for melt 128 is above 1,200° C, and for melt 204 it is about 1,025° C. As the data in table 3 show, the liquidus of melt 201 is above 1,450° C.

Corundum field.—The presentation of the corundum field, as shown in figure 2, is based in part on the data in table 1 and in part on the X-ray identification of alpha alumina as the primary phase in melts 258, 260, and 273 (table 3). Furthermore, the X-ray data and the results of quenching tests support the assumption that $PbO.Al_2O_3$,

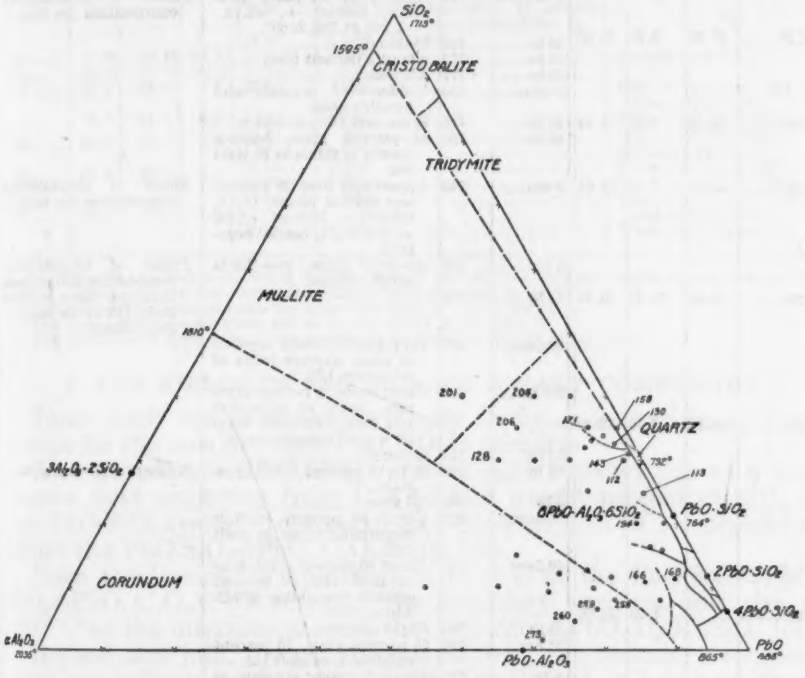

FIGURE 2.—*The system* PbO-Al_2O_3-SiO_2.

The open circles indicate most of those compositions investigated containing less than about 80 percent of PbO. The filled circles indicate the compound compositions. The value of 1,595° C for the Al_2O_3-SiO_2 eutectic is taken from J. F. Schairer, J. Am. Ceram. Soc. 25,241 (footnote 57) (1942).

and also the unidentified phase in melts 258, 259, 260, and 273, melt incongruently to form corundum and glass. The corundum boundary, as drawn in figure 2, extends from 50 percent of Al_2O_3 in the Al_2O_3-SiO_2 system to 10 percent of Al_2O_3 in the PbO-Al_2O_3 system. Temperatures at the quintuple points along this curve have not been determined, and the only fields of established compounds bordering on the corundum field are those of mullite and of $PbO.Al_2O_3$.

TABLE 3.—*Results of crystallization and quenching tests and X-ray examinations on compositions identified by their Melt Numbers in figure 2*

[Portions of the precrystallized samples were used in all cases for specimens quenched after heat treatments of 5 days or less duration]

Melt No.	Composition (wt)			Quenching tests			Crystalline phases found by X-ray examination
				Heat treatment [a]		Crystalline phases produced	
	PbO	Al_2O_3	SiO_2	*Time*	° *C*		
	%	%	%	2 mo	720	Apparently all platy crystals, biaxial +, α1.72, γ1.765, β1.726, 2v 60°.	Phase of unestablished composition (see table 4).
112[b]	67.50	2.50	30.00	46 hr	760	Sintered	
				19 hr	770	About 5 percent glass	
				19 hr	777	All glass	
				8 days	655	Unidentified crystals and possibly glass.	
113	72.49	2.57	24.94	23 hr	715	Same as at 655°, no fusion	
				46 hr	730	20 percent glass, balance mostly crystals as in melt 112.	
121[c]	59.93	5.06	35.01	3 mo	740	Apparently over 95 percent one crystal phase, platy, refractive indices α1.66, γ1.715, β1.71, biaxial negative.	Phase of unestablished composition (see table 4).
128	49.98	20.05	29.97	4 mo	900	one-third glass, two-thirds small crystals.	Phase of unestablished composition and different than the phase in either melt 112 or in melt 121 (see table 4).
				18 hr	1,200		
				33 days	660	Very small fibrous crystals in glass, average index of refraction 1.71.	
				3.5 mo	740	Glass; about 10 percent crystals, index of refraction 1.72 max, 1.658 min, biaxial −; and trace of quartz.	
130	65.32	2.19	32.49	23 hr	755	Sintered	
				67 hr	790	10 to 15 percent small crystals.	No form of silica present.
				6 hr	805	All glass	
				36 days	670	About 90 percent crystals resembling those in melt 112.	
				49 days	700	About 80 percent crystals as in melt 112; 20 percent crystals resembling 6PbO.Al_2O_3.6SiO_2.	
143	67.75	1.25	31.00	23 hr	720	Slight sintering	
				23 hr	725	25 percent glass, 75 percent crystals, as in melt 112.	
				4 hr	775	About 2 percent crystals, as in melt 112.	
				19 hr	780	All glass	
				1 mo	700	About 50 percent crystals (in glass) resembling phase in melt 112.	
158	63.91	1.00	35.09	36 days	780	80 percent glass, 20 percent quartz.	
				23 hr	1,000	Glass and tridymite	
166	80.14	9.10	10.76	29 days	740		Compound 4PbO.Al_2O_3.2SiO_2 (see table 4).
168	83.97	4.76	11.27	47 hr	712		Compound 8PbO.Al_2O_3.4SiO_2 (see table 4).
175	87.9	6.1	6.0	14 days	750		αPbO and 4PbO.Al_2O_3.2SiO_2.
194[d]	74.28	5.76	19.96	15 days	725	Apparently on phase—prismatic crystals having indices of refraction 1.89 max, 1.79 min.	Compound 6PbO.Al_2O_3.6SiO_2 (see table 4).
				18 hr	805	Well sintered	
				23 hr	809	About 50 percent glass	
				70 hr	812	All glass	
200	84.8	9.6	5.6	45 days	700		Definite pattern but no phases identified.
201	39.92	20.02	40.06	70 days	880	Glass; lathlike crystals having indices of refraction 1.69 max., 1.67 min.; and crystals resembling mullite.	Same as melt 128.
				1 hr	1,450		Mullite.

See footnotes at end of table.

TABLE 3.—*Results of crystallization and quenching tests and X-ray examinations on compositions identified by their Melt Numbers in figure 2*

Melt No.	Composition (wt)			Quenching tests			Crystalline phases found by X-ray examination
	PbO	Al_2O_3	SiO_2	Heat treatment [a]		Crystalline phases produced	
	%	%	%	*Time*	° *C*		
204	49.94	10.00	40.06	70 days	880	Glass and platy crystals resembling those in melt 201.	Same as melt 128.
				18 hr	950	85 percent glass, 15 percent very small crystals.	
				18 hr	1,000	90 percent glass, 10 percent crystals (not mullite).	
				18 hr	1,050	All glass	
206	49.40	15.16	35.44	70 days	880		Same as melt 128.
209	35.72	32.15	32.13	70 days	880		Do.
258	77.2	14.8	8.0	23 hr	900		Definite pattern but no phases identified.
	77.2	14.8	8.0	1 hr	1,150		Trace of αAl_2O_3 in glass.
259	75.5	18.0	6.5	23 hr	900		Same as melt 258 (900°).
				1 hr	1,200		αPbO (and βAl_2O_3?).
260	73.4	22.0	4.6	18 hr	1,000		Same as melt 258 (900°).
				¼ hr	1,300		Trace of αAl_2O_3 in glass.
273	70.4	28.0	1.6	23 hr	900		Lines of both melt 5 (800°) and melt 258 (900°).
				¼ hr	1,300		Trace of αAl_2O_3 in glass.

[a] For the heat treatments involving several weeks or months, the indicated temperatures were held to ±20°C. For the shorter treatments, the temperatures were held to ±0.5°C.
[b] This composition approximates the mole ratio 12PbO: Al_2O_3: $20SiO_2$.
[c] This composition approximates the mole ratio 5PbO: Al_2O_3: $10SiO_2$.
[d] This composition approximates the compound composition 6PbO: Al_2O_3: $6SiO_2$.

2. THE FIELDS OF PbO AND ITS BINARY COMPOUNDS

These fields are shown more clearly in figure 3 than in figure 2, except for the area in which $PbO.SiO_2$ is primary.

Lead metasilicate ($PbO.SiO_2$) *field.*—Figure 2 shows this as a very narrow field extending from 15.4 to 29.6 weight percent of SiO_2, in the PbO-SiO_2 system, to a maximum Al_2O_3 content of 1.7 percent at about the $PbO.SiO_2$-$6PbO.Al_2O_3.6SiO_2$ join.

From the liquidus temperature of 695° C at the $PbO.SiO_2$-$2PbO$-SiO_2-$6PbO.Al_2O_3.6SiO_2$ eutectic, the boundary temperatures rise to 735° C at the intersection with the $PbO.SiO_2$-$6PbO.Al_2O_3.6SiO_2$ join.

Beyond this join, toward the quartz field, the boundary compositions are believed to be very nearly as indicated, it being relatively simple to establish the composition limits in which the metasilicate is primary. Little is known in detail, however, regarding the boundary temperatures.

Lead orthosilicate ($2PbO.SiO_2$) *field.*—This field extends from 8.2 to 15.4 weight percent of SiO_2, in the PbO-SiO_2 system, to a maximum Al_2O_3 content of 2.3 percent at the $2PbO.SiO_2$-$8PbO.Al_2O_3.4SiO_2$-$4PbO.Al_2O_3.2SiO_2$ quintuple point. The details are shown in figures 3 and 4.

Tetralead silicate ($4PbO.SiO_2$) *field.*—$4PbO.SiO_2$ is primary in a very small composition area, extending from 6.7 to 8.2 weight percent of SiO_2 in the PbO-SiO_2 system, to 1.2 percent of Al_2O_3 at the $4PbO.SiO_2$-$8PbO.Al_2O_3.4SiO_2$-$2PbO.SiO_2$ eutectic. The $4PbO.SiO_2$-$8PbO.Al_2O_3.$-$4SiO_2$ boundary temperatures rise to 700° C at the intersection with the join.

PbO *field.*—The boundary of the PbO field extends from 6.7 weight percent of PbO in the PbO-SiO_2 system to the PbO-$4PbO.Al_2O_3.2SiO_2$-$PbO.Al_2O_3$ eutectic (fig. 3), and then rises to 865° C at 94 percent of PbO in the PbO-Al_2O_3 system.

$PbO.Al_2O_3$ *field.*—The limits of this field, and the boundary temperatures, are fairly well established where the field contacts those of PbO and of $4PbO.Al_2O_3.2SiO_2$, but the location and nature of the remaining limits are largely based on assumptions. From the $PbO.Al_2O_3$-PbO-$4PbO.Al_2O_3.2SiO_2$ eutectic, the boundary temperatures rise in the direction of decreasing PbO content to about 837° C at the contact with the field of an unidentified ternary compound, then rise through the point *A* (fig. 3) to approximately 1,000° C at 90 percent of Al_2O_3 in the PbO-Al_2O_3 system.

The + symbols in figure 3 indicate compositions for which differential heating curves were obtained. These curves were helpful in establishing the $PbO.Al_2O_3$-PbO-$4PbO.Al_2O_3.2SiO_2$ eutectic.

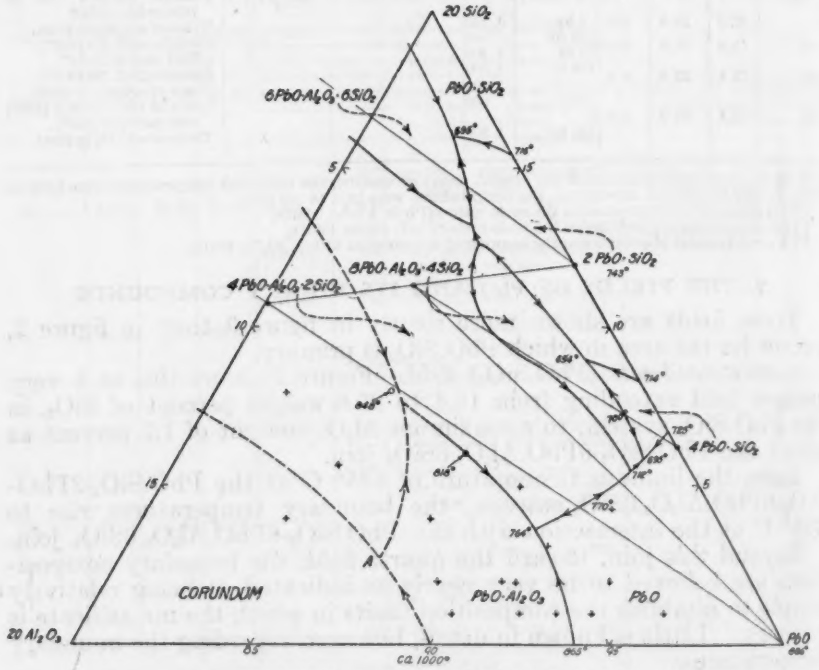

FIGURE 3.—*High* PbO *portion of the* PbO-Al_2O_3-SiO_2 *system.*

This portion of the system contains 9 of the 10 established quintuple points and 2 of the 3 established ternary compounds

3. FIELDS OF THE TERNARY COMPOUNDS

The composition, melting point, and crystallographic properties of three ternary compounds were determined, but it is practically certain that there are at least four more ternary compounds in the system.

$8PbO.Al_2O_3.4SiO2$.—This compound crystallizes as platy laths, characterized by their light-brown appearance when viewed with transmitted light. The refractive indices are 2.08 max and 2.04 min. Optical character was not obtained petrographically.

The X-ray pattern (table 4) is too complex for analysis (H. F. McMurdie).

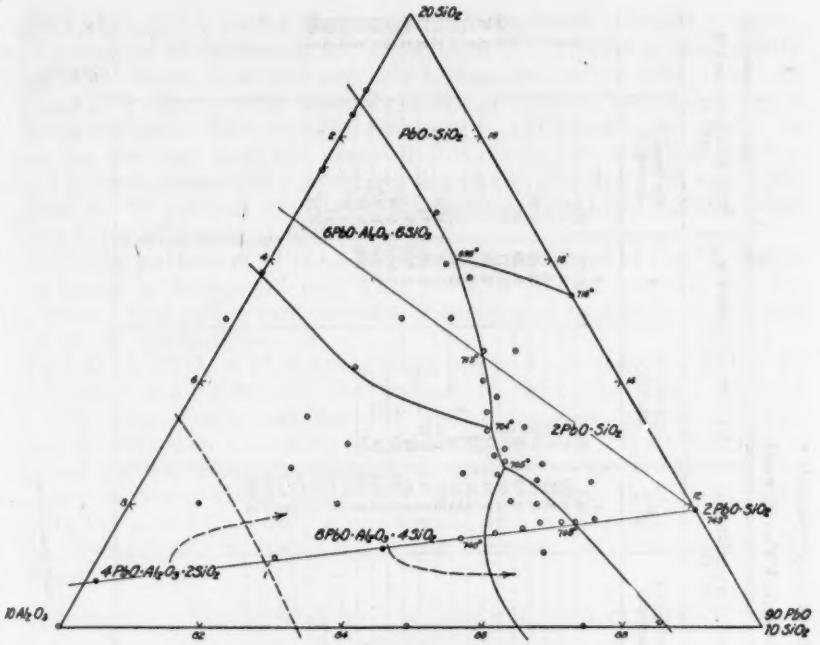

FIGURE 4.—*Detail of the* PbO-Al_2O_3-SiO_2 *system.*

The major portion of the investigation was confined to studies of the compositions, indicated by open circles, in this portion of the system.

$8PbO.Al_2O_3.4SiO_2$ is the only ternary compound for which the entire stability field is known (fig. 3). Critical boundary temperatures are shown in figures 3 and 4, and the compositions of the quintuple and eutectic points are given in table 5. The compound melts incongruently at about 735°±5° C to form $4PbO.Al_2O_3.2SiO_2$ and liquid. The reforming of $8PbO.Al_2O_3.4SiO_2$ is very sluggish (a sample quenched from 745° C, and which was about 50 percent glass and 50 percent $4PbO.Al_2O_3.2SiO_2$, contained no crystals of $8PbO.Al_2O_3.4SiO_2$ after holding for 47 hours at 720° C.) As a result, $4PbO.Al_2O_3.2SiO_2$, which forms during the initial crystallization of a sample, may remain as such; for example, a portion of the original melt was converted to over 90 percent of $8PbO.Al_2O_3.4SiO_2$ by holding at 700° C for 1 month, but some well-developed platy crystals of $4PbO.Al_2O_3.2SiO_2$ were present. In fact, no sample consisting entirely of $8PbO.Al_2O_3.4SiO_2$ was obtained, and this explains why the incongruent melting point was only approximated. The given temperature (735°±5° C) is based in part on results of quenches and in part on the clearly defined liquidus at the intersection of the extended $8PbO.Al_2O_3.4SiO_2$-$4PbO.Al_2O_3.2SiO_2$ join with the boundary for these phases.

$4PbO.Al_2O_3.2SiO_2$.—The area of primary crystallization for this compound probably lies within the bounds of figure 3. The compound was still the primary phase for a melt in the 5 percent Al_2O_3 composition series containing 81.8 percent of PbO but, in a melt containing 79.9 percent of PbO, in the same series, a crystal having indices 1.92 max and 1.83 min was primary.

TABLE 4.—*Diffraction data for the ternary compounds* [a]

[*VS*=very strong; *S*=strong; *M*=medium; *W*=weak; *VW*=very weak]

$4PbO.Al_2O_3.2SiO_2$			$8PbO.Al_2O_3.4SiO_2$		$6PbO.Al_2O_3.6SiO_2$		Melt 112 crystallized at 720° C		Melt 121 crystallized at 740° C		Melt 128 crystallized at 900° C	
Estimated intensity	*d*	*hkl* [b]	Estimated intensity	*d*	Estimated intensity	*d*	Estimated intensity	*d*	Estimated intensity	*d*	Estimated intensity	*d*
	A 7.7			*A* 9.8		*A* 8.6		*A* 9.1		*A* 10.0		*A* 6.59
M	4.43	100	*W*	8.8	*M*	6.74	*M*	8.02	*S*	8.56	*S*	5.85
VW	3.99	110	*W*	4.30	*M*	4.40	*W*	3.45	*S*	3.70	*M*	4.63
W	3.82	111	*VW*	3.26	*W*	3.55	*VS*	3.09	*VW*	3.48	*W*	3.94
W	3.22	200	*VS*	3.05	*VS*	3.30	*M*	2.93	*VS*	3.29	*VW*	3.81
VS	2.95	112	*M*	2.75	*S*	3.03	*W*	2.69	*W*	3.11	*M*	3.63
W	2.86	202	*M*	2.61	*VW*	2.75	*VW*	2.61	*VW*	2.88	*W*	3.47
W	2.76	210	*W*	2.46	*VS*	2.62	*W*	2.58	*M*	2.73	*VS*	3.29
S	2.46	211	*W*	2.36	*M*	2.37	*M*	2.45	*M*	2.66	*VS*	3.01
M	2.33	212	*VW*	2.165	*M*	2.31	*VW*	2.37	*VW*	2.51	*M*	2.91
W	2.24	004	*W*	1.992	*W*	2.070	*W*	2.34	*VW*	2.40	*VW*	2.77
VW	2.19	302	*VW*	1.886	*S*	2.013	*M*	2.26	*W*	2.268	*M*	2.56
VW	2.12	220	*S*	1.735	*W*	1.963	*VW*	2.079	*M*	2.052	*S*	2.47
S	1.964	213	*S*	1.648	*M*	1.878	*W*	2.021	*W*	2.000	*VW*	2.42
M	1.924	303	*W*	1.573	*VW*	1.795	*M*	1.916	*M*	1.905	*VW*	2.35
S	1.819	312	*W*		*W*	1.769	*VW*	1.875			*VW*	2.31
W	1.783	214			*M*	1.711	*W*	1.823			*M*	2.22
S	1.744	402			*W*	1.683	*W*	1.753			*VW*	2.06
M	1.720	320			*VW*	1.659	*W*	1.729				
W	1.657	321			*W*	1.624	*S*	1.679				
W	1.635	410			*W*	1.566	*W*	1.643				
W	1.604	403			*VW*	1.533	*W*	1.561				
VW	1.561	224			*M*	1.506						
		412			*W*	1.488						
					M	1.439						
					VW	1.421						
					W	1.398						
					W	1.380						
					VW	1.361						

[a] Data by H. F. McMurdie.

[b] Based on hexagonal cell with $a=8.78$ A and $c=9.48$ A.

$4PbO.Al_2O_3.2SiO_2$ forms platy crystals, which are uniaxial positive, and the indices of refraction are ϵ1.94, ω1.93. It melts incongruently at 837° C to form glass and crystals having indices of refraction 1.89 max and 1.83 min, but the lines of the X-ray pattern were too obscure to be measured. The reverse reaction is comparatively rapid as shown by the fact that the compound composition, which at 845° C was 85 percent glass and 15 percent the phase of index 1.89 and 1.83, reverted to 10 percent glass and 90 percent $4PbO.Al_2O_3.2SiO_2$ after holding it for 47 hours at 830° C.

The X-ray pattern of $4PbO.Al_2O_3.2SiO_2$, crystallized at 740° C (table 4), indicates a hexagonal cell with a=8.78 A and c=9.48 A. By calculation, this cell would contain 2 molecules and have a density of 5.2 (H. F. McMurdie).

$6PbO.Al_2O_3.6SiO_2$.—This compound melts congruently at 811° C. The crystals are prismatic, the indices of refraction are 1.89 max and 1.79 min, extinction parallel and elongation negative. The limited information regarding its field of primary crystallization is indicated by the diagrams (figs. 2, 3, and 4). The location of the boundary between $6PbO.Al_2O_3.6SiO_2$, and the phase that is primary in melts 112 and 113 is only approximate and incomplete.

The X-ray pattern (table 4) is too complex for analysis (H. F. McMurdie).

4. TERNARY COMPOUNDS OF UNDETERMINED COMPOSITION

Melt 112 (fig. 2), after having been held for 2 months at 720 ±20 °C, had crystallized into large, platy crystals of irregular fracture having indices of refraction α1.72, γ 1.765, β 1.728, the character is biaxial positive, $2v$ about 60°. The diffraction data are given in table 4. The sample appeared to be one phase and the melting was fairly sharp; 760° C for 46 hours produced only sintering, but after 19 hours at 777° C and quenching, the specimen was all glass (table 3). Melt 112 contained PbO, Al_2O_3, and SiO_2, in the molar ratio of 12:1:20. The same crystalline phase was primary in melts 113 and 143.

Melt 121, however, has a markedly different phase in equilibrium at the liquidus. After holding a specimen at 740° ±20° C for 3½ months, it apparently was over 95 percent one crystalline phase tending to platy fracture, with indices of refraction α 1.66, γ 1.715, β 1.71, and biaxial negative in character. This melt approximates the molar composition $5PbO:Al_2O_3:10SiO_2$, and the X-ray pattern of the crystal phase developed at 740° C is described in table 4. The crystals contained inclusions of nicely developed quartz. After the same crystallizing treatment (3.5 months at 740° ±20° C), melt 130 was 90 percent glass and 10 percent well-developed crystals, which have the same optical properties as the crystalline phase in melt 121.

These two phases, together with $6PbO.Al_2O_3.6SiO_2$ and the phases referred to in the discussion of the $4PbO.Al_2O_3.2SiO_2$ compound, form a fringe along the "no man's land," which extends at least to the mullite and corundum boundaries. According to the information in table 3, the phase in melt 128 is present also in melts 201, 204, and 206, indicating that it may be the primary phase for a considerable portion of this superficially investigated region. Also, the results for melt 201 indicate that it may melt to form mullite and glass. This crystalline phase is tabular, has approximate indices of refraction of 1.70 max and 1.69 min, and the diffraction data are given in table 4.

Some of the difficulties which the explorer of this region may expect to encounter are evidenced by the time required to crystallize even partially melts such as No. 130, the volatilization of PbO when crystallization is attempted at temperatures in excess of the melting point of PbO, and the poor crystal development which often makes it impossible to identify phases petrographically even after 2 or more months of heat treatment. Furthermore, it is highly probable, from index of refraction data, that solid solution takes place between a number of the compounds, and that they are (similar to $PbO.Al_2O_3$) unstable below their true melting point.

5. COMPOSITIONS AS GLASSES

Figure 5 presents diagrammatically the information obtained on indices of refraction of the melts as glasses. In those compositions containing more than about 94 percent of PbO, the crystallization of the lead oxide was so rapid that clear glasses were not produced. All the melts appeared to be stable in air and, as is evident from their rates of crystallization, the viscosity in the molten state increased rapidly with increase in silica and in alumina.

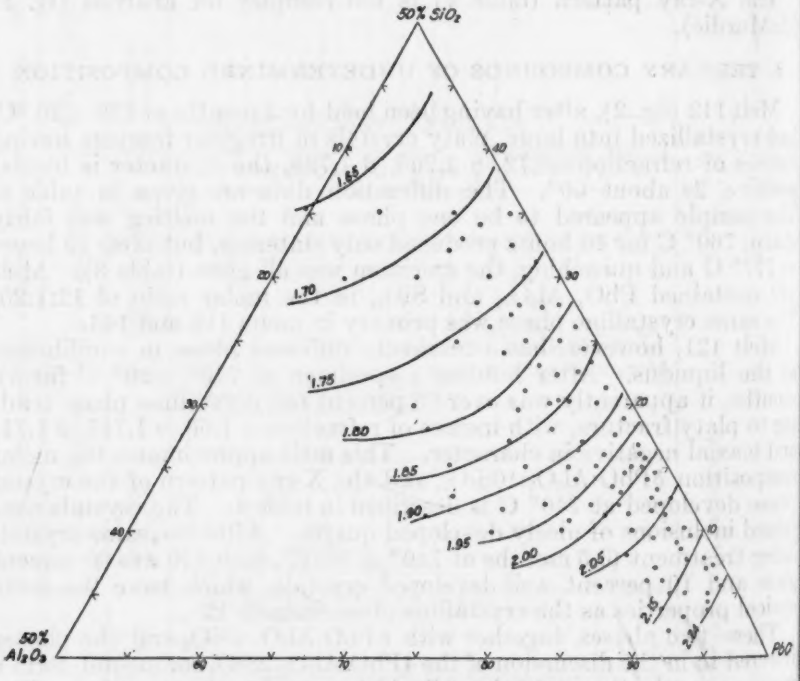

FIGURE 5.—*Index of refraction of compositions as glasses.*

TABLE 5.—*Composition, liquidus, and optical properties of established compounds, quintuple points, and eutectics in the systems* PbO-Al_2O_3 *and* PbO-Al_2O_3-SiO_2

COMPOUNDS

Crystalline phases in equilibrium	Composition (wt)			Liquidus
	PbO	Al_2O_3	SiO_2	
	Percent	*Percent*	*Percent*	*°C*
$PbO.Al_2O_3$	68.64	31.36	----------	About [b]1,000
$8PbO.Al_2O_3.4SiO_2$	83.92	4.79	11.29	[b] 735 ±5
$4PbO.Al_2O_3.2SiO_2$	80.08	9.14	10.77	[b] 837
$6PbO.Al_2O_3.6SiO_2$	74.34	5.66	20.00	811

QUINTUPLE POINTS, NOT EUTECTICS

$2PbO.SiO_2$-$8PbO.Al_2O_3.4SiO_2$-$4PbO.Al_2O_3.2SiO_2$	85.1	2.3	12.6	705
PbO-$8PbO.Al_2O_3.4SiO_2$-$4Pbo.Al_2O_3.2SiO_2$	92.9	1.6	5.5	712
$PbO.Al_2O_3$-$4PbO.Al_2O_3.2SiO_2$-?	85.7	6.8	7.5	837
$PbO.Al_2O_3$-Al_2O_3-?[a]	87.0	10.0	3.0	About 765

EUTECTICS

PbO-$PbO.Al_2O_3$	94.0	6.0	----------	865
SiO_2-$PbO.SiO_2$-?	70.7	1.0	29.3	About 725
$PbO.SiO_2$-$2PbO.SiO_2$-$6PbO.Al_2O_3.6SiO_2$	82.6	1.4	16.0	695
$2PbO.SiO_2$-$6PbO.Al_2O_3.6SiO_2$-$4PbO.Al_2O_3.2SiO_2$	84.6	2.2	13.2	704
$2PbO.SiO_2$-$4PbO.SiO_2$-$8PbO.Al_2O_3.4SiO_2$	89.8	1.2	9.0	694
$4PbO.SiO_2$-PbO-$8PbO.Al_2O_3.4SiO_2$	93.1	1.1	5.8	695
PbO-$4PbO.Al_2O_3.2SiO_2$-$PbO.Al_2O_3$	91.2	5.2	3.6	764

Compound	Optical properties
$PbO.Al_2O_3$	Uniaxial negative ϵ1.85, ω1.91.
$8PbO.Al_2O_3.4SiO_2$	Index of refraction max 2.08, min 2.04.
$4PbO.Al_2O_3.2SiO_2$	Uniaxial positive ϵ1.94, ω1.93.
$6PbO.Al_2O_3.6SiO_2$	Index of refraction max 1.89, min 1.79.

[a] The composition is estimated.
[b] Incongruent melting.

V. SUMMARY

A report is given on the phase relations in the systems PbO-Al_2O_3, and PbO-Al_2O_3-SiO_2.

It is reasonably certain that the compound $PbO.Al_2O_3$ exists, that it is unstable at temperatures in excess of about 970° C, that it breaks down to form corundum and glass, and that it forms a eutectic with PbO (at about 94 percent of PbO) melting at 865° C.

The fields of corundum and of mullite appear to dominate the ternary diagram, with the silica field as a narrow strip extending along the PbO-SiO_2 side of the diagram. Three ternary compounds, and 10 quintuple points, which include 6 eutectics, were found in compositions containing over 70 percent of PbO.

The compound $8PbO.Al_2O_3.4Si_1O_2$ melts incongruently at 735° ±5° C to form the compound $4PbO.Al_2O_3.2SiO_2$ and liquid. The latter compound melts incongruently at 837° C to form a ternary compound of undetermined composition, and liquid. This compound, in turn, may break down to form corundum and liquid. The third established ternary compound is $6PbO.Al_2O_3.6SiO_2$, which melts congruently at 811° C. The liquidus temperatures of the quintuple points range from 694° to 837° C. Three of the eutectics melt within 1° of 695° C

and within 0.2 percent of 1.2 percent of Al_2O_3 in composition; their PbO contents are 82.6 percent, 89.8 percent, and 93.1 percent, respectively.

A considerable portion of the system remains to be investigated. The indications are that at least four more ternary compounds exist in addition to those identified.

In addition to the above, the melting point of Al_2O_3 was redetermined and found to be 2,035° ±10° C, and a chart is presented to show the indices of refraction of the various compositions as glasses.

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COLOR DESIGNATIONS FOR LIGHTS

By Kenneth L. Kelly [1]

ABSTRACT

An extension of the ISCC-NBS (Inter-Society Color Council-National Bureau of Standards) system of color names for the description of the colors of drugs and medicines, has been made for describing the colors of lights. The color names consist of hue names, such as red, pink, yellowish green, or purple, without further modifiers, since they are intended to differentiate lights chiefly according to hue. The hue names are among those used in the ISCC-NBS system and carry the same meaning. The chromaticity ranges identified by each of these hue names are defined by areas on the ICI chromaticity diagram. Comparisons are made between the centers of the proposed hue-name ranges and similar values by other authorities, and with the standard colors recognized in various specifications for marine, railway, aviation, and traffic signal colors.

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I. INTRODUCTION

The development of the ISCC-NBS (Inter-Society Color Council-National Bureau of Standards) system of color names for the description of the colors of drugs and medicines [1, 2][2] suggested to the author the possibility of adapting the same system of names to the description of colors of other than drugs and medicines. In this paper the possibility of applying this system to the colors of self-luminous sources is explored in the hope of offering a basis for the resolution of the conflicting terminology now used for flares, fluorescent and phosphorescent materials, and signal lights. This system could not displace precise specifications in terms of either chromaticity coordinates or standard filters such as are used for railway signal lights [3], but it is expected to provide color names recognized by the general public as appropriate. The spacing of the color-name boundaries is based on that of the ISCC-NBS system [1]; but the shape of

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[2] Figures in brackets indicate the literature references at the end of this paper.

the boundaries is based on the extensive data collected by the OSA subcommittee [4] on the spacing of the Munsell colors. Both spacing and shape have been modified in accordance with observations by two observers.

II. GENERAL PLAN

The suggested system of color names is composed of 19 hue names and three names indicating reddish hues of reduced saturation (orange pink, pink, and purplish pink). There are, however, no modifiers used to designate whether a light is bright or dim or strong, analogous to what is done for surface colors, because it is intended that the names shall apply to a fairly wide range of intensities and retinal adaptive conditions [5]. The changing of the intensity of the source in a source-filter combination will in some instances change the hue (the Bezold-Brücke [6] phenomenon) of the perceived color sufficiently to require the application of another color name, whereas in others the modified hue will remain in the same color-name segment. The boundaries adopted are intended to define chromaticities to which the names apply under the most common conditions of use.

The designations included in this system are red, reddish orange, orange, yellowish orange, yellow, greenish yellow, yellow-green, yellowish green, green, bluish green, blue-green, greenish blue, blue, purplish blue, bluish purple, purple, reddish purple, red-purple, purplish red, purplish pink, pink, and orange pink. All of these are names used in the ISCC–NBS system for light colors of surfaces. The hue names (such as brown or olive) used for dark colors of surfaces are not appropriate for self-luminous sources.

The ISCC–NBS hue-name boundaries are specified in terms of the standards in the Munsell Book of Color [7], and it was therefore decided to base the hue-name boundaries of the proposed system on a study of the high-chroma Munsell samples in an attempt to make each of the proposed hue-name ranges include the same range of hue as for the surface color names. It was soon found that even the strongest Munsell samples would not extend these boundaries far into the region on the ICI diagram representing the lights to be designated. Recourse was then had to the constant-hue loci given in the final report [4] of the OSA subcommittee on the spacing of the Munsell colors based on the data contained in the recent paper by Kelly, Gibson, and Nickerson [8]. These curves are based on the Munsell standards and are extrapolated out to the spectrum locus by smooth curves. The minimum and maximum saturation boundaries of the pinks were also determined with the aid of the Munsell standards.

III. EXPERIMENTAL CHECKS

The locations of the several hue-name boundaries on the ICI chromaticity diagram were checked by two independent series of observations. The first check consisted in observing a series of light filters available at the National Bureau of Standards in connection with the specification of various signal colors. The colorimetric specifications of these filters were known in combination with a source at 2,842° K. From these specifications the designation was found for each source-filter combination, and the observer judged whether the designation was appropriate to the light transmitted by the filter

illuminated by a source at approximately this color temperature. Boundaries in the blue and purple region, some in the red, and several elsewhere were adjusted to accord with these judgments. Light filters were not, however, available for all portions of the diagram, and certain of the boundaries remained unchecked by this method.

The colorimetric specifications of the Lovibond glasses [9] for a source of color-temperature 2,842° K are being computed at the Bureau, and the specifications of sufficient combinations of these glass filters have been completed to yield a preliminary network indicating approximately the chromaticities of these glasses and their combinations on the ICI chromaticity diagram. From this network it is now possible to determine with sufficient accuracy which glass or set of glasses will, in combination with a source at 2,842° K, give a colored light whose colorimetric specification will plot at a specified point on the hue-name diagram. In the second check, a number of these combinations were viewed in a darkened room and judgments were made by two observers (KLK, DBJ [3]) as to which of the hue names listed above was the most appropriate. In this manner it was possible to check most of the boundaries throughout their length and to obtain sufficient points on the other boundaries so that they could be drawn with fair accuracy. Through the use of the Lovibond glasses it was possible to extend these constant-hue lines far beyond the strongest Munsell samples.[4]

IV. DEFINITION OF THE DESIGNATIONS ON THE CHROMATICITY DIAGRAM

The chromaticity ranges identified by each of the color names for lights are defined by areas on the ICI chromaticity diagram [10], see figure 1. The constant-hue boundaries, if extended, would pass through the point representing ICI standard illuminant *C*, which is approximately in the center of the diagram. Around this point, corresponding to daylight surface colors of low saturation, is a region within which no color names have been assigned in this system. Bounding this region is a line representing the weakest colors that will receive a color name, and between this minimum line and the spectrum locus are the areas to which are assigned the color names offered in this paper. The region called orange pink, pink, and purplish pink lies between the central region and the purple, red, and orange segments.

V. DISCUSSION

It must be remembered that the determination of the hue-name boundaries, which are constant-hue curves, does not constitute a redetermination of the psychologically unitary colors, or "Urfarben", described by Dimmick [11, 13], since the boundaries describe the colors that appear to fall equally between two named hues, for example, between red and reddish orange. However, it is possible to estimate from these limits the dominant wavelengths of the chromaticities of maximum purity corresponding to the unitary hues, and

[3] Deane B. Judd, National Bureau of Standards, Washington, D. C.

[4] The points so determined and the lines connecting them have been accepted by the OSA subcommittee and are included in their final report [4].

these values are shown in table 1, together with values previously reported by various authortities [11, 12, 13] arranged in chronological order. Many of the authorities quoted find unitary red among the spectrum colors but the most careful recent determination finds all spectrum reds to be slightly yellowish, and unitary red must for this

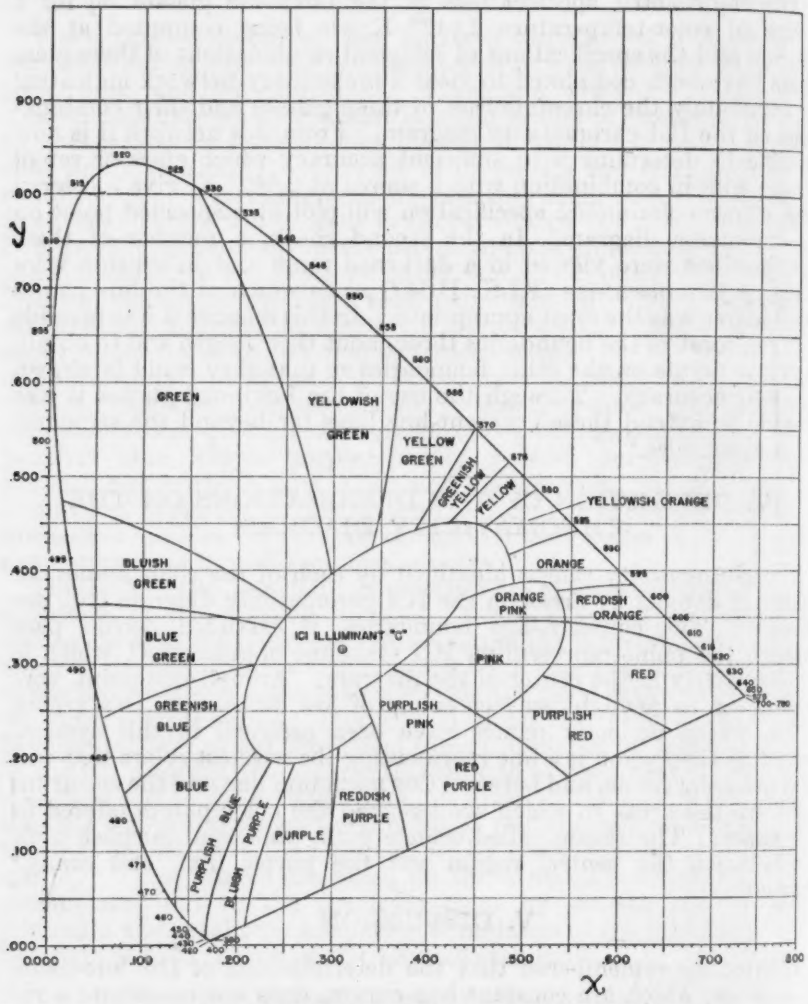

FIGURE 1.—*Suggested definitions of color designations for self-luminous sources.*

The chromaticities for each designation are indicated on the chromaticity diagram of the standard ICI coordinate system for colorimetry [10]. Spectrum chromaticities are also shown, the wavelengths being indicated in millimicrons.

determination be specified by the complementary wavelength. So that this recent determination may be compared to the previous determinations and an average computed, complementary wavelengths are given in table 1 in parentheses following the values of dominant wavelengths. The averages of the wavelengths for the unitary hues are equally weighted arithmetical means.

TABLE 1.—*Dominant wavelengths (millimicrons) corresponding to various hues*

TABLE 1.—*Dominant wavelengths (millimicrons) corresponding to various hues*

Authority	Date	Red	Reddish orange	Orange	Yellowish orange	Yellow	Greenish yellow	Yellow-green	Yellowish green	Green	Bluish green	Blue-green	Greenish blue	Blue	Purplish blue	Blue-violet	Violet	Bluish purple	Purple	Reddish purple	Red-purple	Purplish red
Helmholtz	1866	687 (492. 4c)	656							527						431						
Bezold	1874		656		589	578		558		532		502		468		432						
Donders	1884					582				535				485								
Rood	1890	700 (492. 4c)	621	597	588	581				527		502		473		438	406					
Voeste	1902					577				498				476								
v. Kries	1907					574				503												
Westphal	1909					574				506				479								
Dreher	1911					575				509				477								
Ridgway	1912	644 (492. 1c)		598		577				520				473			410					
Goldytsch	1916													468								
Bradley	1920	656 (492. 2c)		608		579				514				469			421					
Goldmann	1922					568				504				468								
Priest	1926	680 (492. 4c)				583				515				475								
Brückner	1927					578				498				471								
Shubert	1928					574				500				467								
Purdy	1931					576				504				476								
Drever	1932		640			568				508				471								
Weld	1932		622		597			577				492				456						
Gage	1933		625		600																	
Ornstein	1934			596		575		562		515		492		475								
Verbeek	1935		605	598	587	580		569		530		496										
Terpstra	1935		604	592	585	577		563		510		487		470		440						
Seguy	1936	700 (492. 4c)		597		581				527				473		438	406					
Dimmick	1939	493. 6c				582				515				476								
Averages		492. 5c	629	598	591	577		566		514		495		474		439	411					
Proposed system	1943	493c	606	592	583	578	573	565	545	508	495	490	485	476	454			566c	560c	545c	506c	496c

These averages of wavelengths for the various hues also are compared in table 1 with the wavelengths corresponding to the centers of the proposed hue ranges at the edges of the diagram (fig. 1). It will be noted that the agreement for red, yellow, yellow-green, green, and blue is good, but that for reddish orange, orange, and yellowish orange somewhat inferior. Only four values have been previously reported for violet and none for the purples; so it is impossible to make any comparisons with these data in the purplish blue to red region. From the wavelengths reported, blue-violet and violet fall between the centers of the suggested purplish blue and bluish purple areas. Except for yellowish orange, the suggested system gives wavelengths intermediate to those reported by the various authorities for the corresponding hues.

In table 2 the chromaticity ranges of these proposed color designations are compared with those defined in the standard specifications for the several marine [14], traffic [15], railroad [3], and aviation [16] signal-light colors. The colors of lights permitted by the specifications are grouped in table 2 according to hue, and opposite them in the next column are given the corresponding proposed color designation or designations. It will be noted, for example, that ANC [16] (Army, Navy, Civil Aeronautics Administration) aviation red includes not only chromaticities described here as red, but also some described as reddish orange. This is correct, since the orange limit of aviation red is the color of light from a neon discharge tube, which is reddish orange. ANC identification yellow is quite reddish so as to be distinguishable from the color of the incandescent lamp (which is often called "white"). Because of its reddish hue, the name orange might be more appropriate than yellow to describe the color of this signal. The color designation "amber" has sometimes been used for yellow signal colors. The railroad, marine, and traffic signal-green chromaticity ranges have been purposely inclined toward bluish green so as to be distinguishable from yellow and red signal lights by a red-green-blind observer; the name bluish green is quite suited to part of this range. Although the standard specifications for railroad signal blue and aviation blue spread into the bluish purple area, the lights actually used would be called by this system either blue or purplish blue.

TABLE 2.—*Comparison of formal color specifications with the proposed color names*

Color specification	Color name in proposed system	Remarks
Marine and traffic signal red	Red	
Railroad signal red	do	
Railroad highway crossing red	Red and reddish orange	
ANC aviation red	do	Neon light is one limit and would be called reddish orange.
ANC identification red	Red	
Marine and traffic signal yellow	Yellowish orange and orange	
Railroad signal yellow	Orange	
ANC aviation yellow	Yellowish orange and orange	
ANC identification yellow	Reddish orange and orange	
Marine and traffic signal green	Green and bluish green	Colorblind see this as nearly neutral.
Railroad signal green	do	
ANC aviation green	Yellowish green, green, and bluish green.	
ANC identification green	Yellowish green and green	
Railroad signal blue ANC aviation blue	Blue, purplish blue, and bluish purple.	Actual signals are either blue or purplish blue.
Railroad signal purple	Purplish blue, bluish purple, and purple.	Railroad signal purple is not used as a chromaticity term in the usual sense but designates a spectral composition separated into red and blue components by the chromatic aberration of the eye.

Thus from the tables, the agreement of these data both with the previously reported data for unitary and other hues and with the names used in the standard specifications, although not perfect, is fairly good. It must be remembered in this connection that the suggested system embodies a greater number of color names than were used in previous studies of signal-light color systems, such as those by McNicholas [17] and Holmes [5]. In those studies a limited number of color names was allowed, and each name therefore applied to a wide range of hue. These ranges were selected for maximum visual contrast between adjacent named color ranges, and they apply to signal-light systems of the corresponding number of colors. The names applied to the ranges, however, are somewhat arbitrary and not necessarily true descriptions of the color ranges selected. The suggested system, on the other hand, is intended to provide appropriate color names for the colors of all self-luminous bodies. However, considerable work remains to be done before the diagram defining these color designations can be recommended in final form.

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IRON AS A TANNING AGENT

By Joseph R. Kanagy and Ruth A. Kronstadt

ABSTRACT

Lactic, citric, hydroxyacetic, and gluconic acids were found satisfactory for stabilizing iron solutions to be used for tanning leather. The influence of pH and concentration on the combination of iron (Fe_2O_3) with standard hide powder was investigated. The maximum fixation of 23 to 25 percent of ferric oxide occurs in the pH range 3.5 to 4.0. Practical tanning experiments were made with goat- and calf-skins. The shrinkage temperatures of the iron-tanned leathers are lower than those of well-tanned chrome leathers. The results of accelerated aging tests indicate that all of the iron-tanned leathers tested had at least fair aging qualities except where gluconic acid was used. The use of iron salts for replacing those of chromium in the tanning of leather shows most promise where citric acid is used for stabilizing the solutions.

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I. INTRODUCTION

This report gives the results of a study of the use of iron salts for tanning light leathers used in the manufacture of shoes and garments for military and civilian use. The investigation includes a study of the properties of the iron tanning solutions, an improved method for tanning the leather, and a determination of the resistance of the leather to an accelerated aging test. This test was developed recently and consists in heating the leathers at 100° C. in the presence of moisture.

The investigation was undertaken at this time of national emergency because of the shortage in the domestic supply of tanning materials. The effect of this shortage is intensified by the demands of industries other than the leather industry, on material which is used in tanning. This is well illustrated in the case of chromium, which has extremely important uses in the manufacture of metal alloys for war industries and in the case of phenols, used for synthetic tanning materials, which are necessary to produce an increasing amount of synthetic resins and plastics.

The possible replacement of chromium by iron in tanning is shown by the results of past investigations. There are plentiful domestic supplies of iron. These facts suggested advantages to be gained by further studies in tanning with iron. The results given in this report show considerable promise for the use of iron salts in place of those of chromium in leather manufacture.

Literature references and a discussion of the work of others on the use of iron salts for tanning are included as a guide for those who may wish to review previous work. Tests of the properties of the iron tanning solutions are described. Experimental data are given on these tests and also on those applied to prepared leathers.

II. REVIEW OF PREVIOUS WORK

As early as the eighteenth century, attempts were made to develop methods of tanning with iron salts. A history of iron tanning is given in a book by J. Jettmar [1].[1] The first recorded patent on iron tanning was that taken out by Johnson, an Englishman, in 1770. Twenty-four years later another English patent was given to Ashton. The ferric salt was prepared either by dissolving iron oxide in acetic acid or by oxidizing ferrous sulfate. Hermbstadt in 1805 studied Ashton's patent and found that the best tannage resulted from the use of iron oxide in acetic acid. This fact is interesting in the light of our present knowledge of the formation of complex ions of organic acids with iron salts.

In 1842 Jules Bordier took out an English patent involving the use of basic ferric sulfate prepared by the treatment of a solution of ferrous sulfate with manganese dioxide or nitric acid, followed by the addition of ferric oxide. Knapp obtained a number of patents on iron tanning, but the use of his methods has failed to produce good leathers. The leather produced was brittle and deteriorated quite rapidly with age. He [2] mentioned also that while the tanning properties of iron were well known, no one as yet had produced a serviceable leather with iron salts.

Several explanations were given for the failures to produce successful iron tannages. Procter [3] suggested that the iron salts were oxygen carriers, and acted as oxidation catalysts to destroy the leather. Casaburi [4] believed that the poor results obtained with iron tannages were due to the failure to remove uncombined ferric salts from the leather. He obtained a complete tannage with a 67-percent acid ferric sulfate, and a less satisfactory result when some ferric chloride was present. With basic ferric chloride the skins became swollen and gelatinized. A better result obtained with basic ferric sulfate may have been due to the fact that it permits less swelling of the skin.

Jettmar [5] found the greatest difficulty in iron tanning to be the proper neutralization of the acid formed in the leather. For comparison, if chrome leather contains too high a proportion of sulfuric acid, it becomes very brittle on drying and assumes a dark-green color. The proper degree of neutralization for chrome leather is easy to achieve, since chromium hydroxide does not precipitate at a low pH value. In neutralizing iron-tanned leather, however, Jettmar found that the iron salts were colloidally dispersed and were washed out of the leather.

[1] Numbers in brackets indicate the literature references at end of this paper.

Jackson and Hou [6] made an extended study of the various factors involved in the iron tanning of sheep skins, including the best method of oxidizing ferrous to ferric salts and the relation of basicity or acidity of the ferric salt to its stability and tanning properties. They prepared an iron-tanned leather which they were convinced compared favorably with other mineral-tanned leathers. It would not stand the boiling test, but shrank in water at temperatures greater than 75° C. They claimed that the chief cause of brittleness in iron-tanned leather was not the oxidizing action of the ferric salts, but rather an improper method of tanning, resulting in the precipitation of hydrated ferric oxide.

Thomas and Kelly [7] made a theoretical study of the factors involved in iron tanning, applying principles such as those used in alum and chrome tanning. They studied the effect of basicity on the amount of iron fixed by hide substance at different concentrations for different lengths of time. The influence of the neutral salts, sodium chloride and sodium sulfate were also considered.

From our present-day knowledge it is not expected that any of the above methods could be successful in preparing a satisfactory leather with fair aging characteristics, because the pH of the leather they produce is too low. The difficulty which was most likely encountered by the investigators was the precipitation of the iron salt on neutralization. Jettmar [5] was probably the first to attempt to make the iron solutions more stable by adding a strong solution of a neutral salt. Reinich in 1892 [4] suggested the addition of salt to iron chloride and afterward (1912) used an iron tanning solution made with iron chloride, magnesium carbonate, and aluminum chloride.

A number of [8] patents have been issued in which polycarboxylic acids, hydroxy acids, and amino acids are used to stabilize the iron solutions by complex ion formation. Other patents [9] cover the use of phosphates of aluminum, chrome and iron, albuminous substances, such as protalbumic acid and urea, and substitution products of ammonia.

Casaburi followed his use of ferric acetate with that of organic acids. He made extensive studies [10, 11, 12] with citric and tartaric acids and claimed the preparation of an iron-tanned leather with citric acid which withstood the boiling test.

The success of other investigators, although somewhat limited, showed the likelihood that better methods for tanning with iron could be developed. It suggested in a large part the course of the present investigation.

III. MATERIALS

A reagent grade ferric sulfate $Fe_2(SO_4)_3 \times H_2O$ was used. It contained approximately 29.5 percent of iron determined as Fe_2O_3 and about 56.6 percent of sulfate calculated as H_2SO_4. The composition of the batches of materials varied slightly.

The acetic and citric acids used were chemically pure grades. The lactic, hydroxyacetic, and gluconic acids were technical grades of 85, 70, and 50-percent strength, respectively.

The sodium carbonate was an anhydrous chemically pure material.

Standard hide powder prepared according to the specifications of the American Leather Chemists Association was ground to pass through a 2-mm sieve in a Wiley mill and used in the fixation experiments.

IV. RESULTS AND DISCUSSION

1. STUDIES OF THE IRON TANNING SOLUTIONS

Ferric hydroxide will be precipitated from solutions of ferric sulfate if a base such as sodium hydroxide or sodium carbonate is added, at a pH of about 2.5. Ferric hydroxide cannot be used for tanning. If, however, an organic acid is added to prevent this precipitation, the resulting solution can be used satisfactorily. The amount of the organic acid required to stabilize the solutions or prevent the precipitation of ferric hydroxide was determined by varying the concentration of the acid in increments of 0.05 and 0.1 of a mole per 1,000 ml of solution.

Tanning solutions were prepared by dissolving 40 g of the reagent grade ferric sulfate and the different amounts of the organic acid in 1,000 ml of solution. One-hundred-milliliter portions of the solutions were treated with different amounts of a 5-percent solution of sodium carbonate and made up to 200 ml. The resulting pH values were within the range 1.5 to 6.0.

It was considered that a sufficient quantity of the organic acid had been added if a slight precipitate of ferric hydroxide remained after 48 hours. The absence of a precipitate usually meant that more than the necessary amount of acid had been added, whereas the presence of a large precipitate obviously meant that too little had been added. By this method the amount of acetic, lactic, citric, hydroxy-acetic, or gluconic acid required to stabilize the tanning solutions were determined and are recorded in table 1. Citric acid is required in the lowest concentration of all the acids listed, whereas acetic is required in the highest concentration.

TABLE 1.—*Amounts of organic acids required to stabilize the iron tanning solutions at all* pH *values in the range 2 to 6*

Acid	Acid per 40 g of $Fe_2(SO_4)_3 x.H_2O$ in 1,000 ml of solution	Concentration
	Grams	*Moles/liter*
Acetic	60	1.0
Lactic	9	0.1
Citric	6.4	.033
Hydroxyacetic	15.2	.2
Gluconic	19.6	.1

The tanning properties of the solutions prepared in this way were determined by placing in them small pieces of steer hide, which were later examined for tannage. Steer hide was used so that the rate of penetration of the iron salt into the skin could be observed. The degree of tanning found by visual inspection indicated that the optimum pH range for tanning was 2.5 to 4.5. Some tanning action occurred throughout the range 1.75 to 5.5. Above or below these limits the hide remained soft and flabby, little combination having occurred. The addition of too much of the organic acid will prevent complete tanning action at any pH.

The changes in the pH on storage of the tanning solutions prepared in this way were determined. These experiments are analogous to others that have been applied to chrome tanning solutions. Iron tanning solutions containing 8 g of ferric sulfate and different amounts

TABLE 2.—*Changes in the* pH *of the iron tanning solutions with time of storage*

TABLE 2.—*Changes in the* pH *of the iron tanning solutions with time of storage*

[Iron tanning solutions containing 8 g of ferric sulfate and different amounts of the organic acid in 100 ml were treated with varying amounts of sodium carbonate or sodium hydroxide and made up to 200 ml. The pH values of the solutions were determined immediately after preparation and after 24 hours and 48 hours.]

Acid	Initial concentration of organic acid	1.2 g of sodium carbonate added			2.0 of sodium carbonate added			2.8 g of sodium carbonate added			3.6 g of sodium carbonate added			4.4 g of sodium carbonate added		
		pH			pH			pH			pH			pH		
		Initial	24 hr	48 hr	Initial	24 hr	48 hr	Initial	24 hr	48 hr	Initial	24 hr	48 hr	Initial	24 hr	48 hr
	g/800 ml															
Lactic	2.1	2.05	2.00	2.00	2.50	2.40	2.40	2.65	2.40	2.40	2.75	2.55	2.55	3.40	3.15	3.15
Do	4.2	1.85	1.80	1.80	2.15	2.15	2.15	2.50	2.50	2.50	3.05	2.85	2.80	3.45	3.10	3.15
Citric	1.3	1.85	1.75	1.75	2.40	2.40	2.35	2.80	2.40	2.35	2.85	2.60	2.55	3.40	3.10	3.05
Do	2.6	1.50	1.45	1.50	1.80	1.80	1.85	2.20	2.20	2.20	2.75	2.75	2.75	3.70	3.25	3.20
Hydroxyacetic	4.3	1.90	1.80	1.85	2.35	2.10	2.10	2.50	2.45	2.40	2.70	2.70	2.65	3.80	3.25	3.15
Gluconic	3.6	1.75	1.75	1.75	2.10	2.10	2.05	2.40	2.30	2.30	3.15	2.75	2.70	3.70	3.30	3.30
		1.0 g of sodium hydroxide added			1.6 of sodium hydroxide added			2.2 g of sodium hydroxide added			2.9 g of sodium hydroxide added			3.5 g of sodium hydroxide added		
		pH			pH			pH			pH			pH		
		Initial	24 hr	48 hr	Initial	24 hr	48 hr	Initial	24 hr	48 hr	Initial	24 hr	48 hr	Initial	24 hr	48 hr
Lactic	2.1	2.10	2.10	2.10	2.55	2.45	2.40	2.80	2.70	2.60	3.20	3.05	3.05	4.30	4.20	4.10
Citric	1.3	1.95	1.95	2.00	2.40	2.40	2.40	2.70	2.60	2.55	2.90	2.85	2.70	3.45	4.35	4.35
Do	2.6	1.20	------	1.30	1.45	------	1.45	2.30	------	2.35	3.00	------	3.00	3.60	------	7.15

of the organic acid in 100 ml were treated with varying amounts of sodium carbonate or sodium hydroxide and made up to 200 ml. The pH values of these solutions were determined immediately after preparation and after 24 and 48 hours of storage. The acidity of most of the solutions increased slightly on aging. Little change was noted after 24 hours. The results are shown in table 2.

A range of minimum stability of the tanning solutions containing an organic acid is shown at about pH 3 to 4.5. This is observed in the presence of the smaller concentrations of the organic acids if either sodium hydroxide or sodium carbonate is added. The solutions are stable at pH values above 4.5 or below 3, a behavior which resembles that of an amphoteric compound. This range becomes narrower on increasing the concentration of the organic acid and disappears entirely if sufficient acid is added. Results illustrating observations on gluconic acid are given in table 3.

TABLE 3.—*Ferric hydroxide, expressed as ferric oxide, precipitated from iron tanning solutions at various* pH *values obtained by the addition of different amounts of sodium carbonate or sodium hydroxide.*

The iron tanning solutions contained 40 g of ferric sulfate [$Fe_2(SO_4)_3 xH_2O$] and the noted amounts of gluconic acid in 1,000 ml of solution

0.05 mole of gluconic acid and Na_2CO_3		0.075 mole of gluconic acid and Na_2CO_3		0.075 mole of gluconic acid and NaOH	
pH	Fe_2O_3	pH	Fe_2O_3	pH	Fe_2O_3
	g		*g*		*g*
1.5	0	1.5	0	1.7	0
2.7	.04	2.6	0	2.5	0
3.3	1.04	2.8	0.48	3.4	0.84
4.6	2.40	4.0	1.24	4.0	.06
5.8	1.16	5.7	0	5.3	0
6.3	0.26	6.0	0	10.3	0

The tanning solutions were also studied by means of electrometric titration curves. Fifty-milliliter aliquots of solutions containing 40 g of ferric sulfate in 1,000 ml or this concentration of ferric sulfate and a definite amount of the organic acid in 1,000 ml were titrated with 1.0 *N* sodium carbonate solution.

The titration curves for the experimental iron tanning solutions, and for solutions of the separate constituents are given in figure 1. The titration curve for sulfuric acid solution equal in sulfate ion content to that of the tanning solutions is also shown.

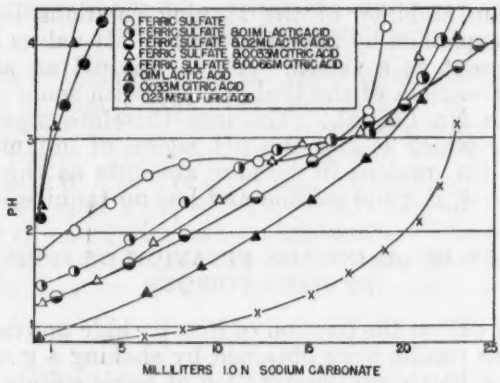

FIGURE 1.—*Comparison of the titration curves.*

The curves represent the materials at the following concentrations: 40 g of ferric sulfate in 1,000 ml; 40 g of ferric sulfate and 10.6 g of technical lactic acid (0.1*M*) in 1,000 ml; 40 g of ferric sulfate and 21.2 g of technical lactic acid (0.2*M*) in 1,000 ml; 40 g of ferric sulfate and 6.4 g of citric acid (0.033*M*) in 1,000 ml; 40 g of ferric sulfate and 12.8 g of citric acid (0.066*M*) in 1,000 ml; 10.6 g of technical lactic acid (0.1*M*) in 1,000 ml; 6.4 g of citric acid (0.033*M*) in 1,000 ml; 22.5 g of sulfuric acid (0.46*N*) in 1,000 ml.

The addition of lactic or citric acid apparently increases the amount of highly ionized acid in the solutions, for, as the concentrations of these acids are increased, the curves approach more nearly that of the sulfuric acid. The citric acid is more effective in this respect than the lactic acid. The curve for the ferric sulfate alone has a slope of zero at a pH of about 2.8. At this pH the iron is completely precipitated. This does not occur in the other solutions, where the iron is not completely precipitated.

A probable explanation of the increase in the amount of titratable acid in the regions of pH less than 3 can be given on the basis of a change in the hydrolysis equilibrium of the ferric sulfate solution through the formation of a complex ion. This equilibrium may be represented by the following equations where La represents lactic acid:

$$Fe_2(SO_4)_3 + 2H_2O \rightleftharpoons 2FeOH\,SO_4 + 2H^+. \quad (1)$$

$$FeOH\,SO_4 + H\,La \rightleftharpoons (FeLa)^{++}SO_4 + H_2O. \quad (2)$$

Equation 1 represents a partial hydrolysis of the ferric sulfate to form a basic salt and hydrogen ions. The $FeOH\,SO_4$ is unstable and slowly hydrolyzes further to form ferric hydroxide which is precipitated. It can then be assumed that the addition of an organic acid, such as lactic (La), will form a complex ion $[FeLa]^{++}$, which is soluble (eq 2), and the reaction represented by equation 1 will be driven further to the right and more hydrogen ions will be formed. This would explain the increase in hydrogen-ion concentration shown by the titration curves.

The addition of too much of the organic acid will decrease the tanning action at low pH values because reaction (2) will be shifted to the right, and little of the iron salt will be left in the form $FeOH\,SO_4$, which is assumed to be the active tanning agent. The formation of a complex ion that results in an increase in acidity also gives a probable explanation for the increase in hydrogen-ion concentration of the solutions on storage, as shown by the results in table 2.

The minimum stability of the tanning solutions between pH 3 and 4 may be explained by assuming that at pH values lower than 4, the iron is present as a cation. Above this pH an anion may be formed by the reaction of the $[FeLa]^{++}$ ion with some of the sodium lactate to form $Na\ Fe(La)_4$. The iron therefore passes through a transition state which is also the pH region of minimum stability. The $Fe(La)^{-}_4$ ion, present in greater amounts as the pH value is increased above 4, is quite soluble and has no tanning effect.

2. EFFECT OF pH ON THE FIXATION OF IRON (Fe_2O_3) BY HIDE POWDER

The effect of pH on the fixation of iron by hide powder is shown in figure 2. These results were obtained by shaking 4 g of the powder for 4 hours in a bottle containing 24 g of ferric sulfate and 6.3 g of lactic acid or 3.9 g citric acid in 600 ml of the solution. The pH was varied by the addition of sodium carbonate. The concentration of ferric sulfate selected was that which gave maximum fixation in simultaneous experiments reported in section IV, 3, where the effect of concentration on the fixation of iron by hide powder is reported.

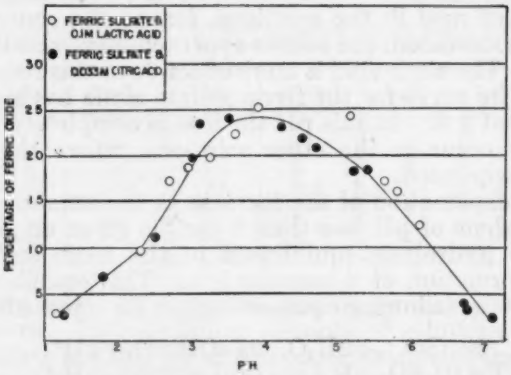

FIGURE 2.—*Variation of the percentage of iron determined as ferric oxide fixed by hide powder, with change in* pH *of the tanning solutions.*

Maximum fixation occurs in the pH range 3.5 to 4.25, where the basicity[2] varies from approximately 0.66 at 3 to 1.0 at 4. The greatest amounts of ferric oxide combined in this region vary from 23 to 25 percent, which is 3 times greater than the results obtained by Thomas and Kelly [7], who made studies at basicities less than 0.33. The smallest amounts of ferric oxide combine at pH 1 and again at pH 7. The results at pH 1 may be attributed to low basicity. The low results at pH 7 are possibly due to the formation of a complex ion that has little tanning action. Similar results were observed when sodium oxalate, which also forms complex ions, was added to chrome liquors [13].

[2] In leather chemistry the term "basicity" is used to express the ratio of the equivalents of base to equivalents of the metallic tanning element. In this case, it is the ratio of equivalents of sodium carbonate to the equivalents of iron.

3. EFFECT OF CONCENTRATIONS ON THE FIXATION OF IRON (Fe_2O_3) BY HIDE POWDER

The results of the studies on the effect of concentration on the fixation of iron by hide powder are shown in figure 3. In these studies, 4 g of the powder was shaken for 4 hours in a bottle containing 4 to 36 g of the reagent grade ferric sulfate and 1.06 g of the technical grade lactic acid or 0.64 g of citric acid for each 4 g of ferric sulfate in 600 ml of solution at a pH of 3.5 to 4.25. The pH values of the solutions were adjusted with sodium carbonate. The pH range for the determinations was selected from a simultaneous study on the effect of pH on the fixation of iron by hide substance (see this section, part 2).

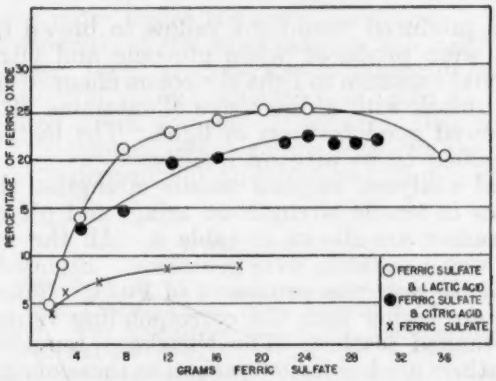

FIGURE 3.—*Variation of the percentage of iron determined as ferric oxide fixed by hide powder at* pH *3.5 to 4.25, with change in concentration of the tanning solutions.*

0.265 g of lactic acid or 0.16 g of citric acid was added for each gram of ferric sulfate ($Fe_2(SO_4)_3 \times H_2O$)

Slightly higher percentages of ferric oxide are fixed by hide powder in the presence of lactic acid than in the presence of citric acid. These percentages show a tendency to decrease at the highest concentrations of ferric sulfate.

The curve representing the effect of ferric sulfate alone is presented to show that increased amounts of iron may be fixed in solutions having higher pH values if precipitation of ferric hydroxide is prevented by the addition of an organic acid. This solution of ferric sulfate prior to being used for tanning was adjusted to the point where a slight precipitate failed to dissolve on mixing. The pH was approximately 2.2 and the basicity 0.125.

4. TANNING EXPERIMENTS

Tanning experiments were made with pickled goatskins and one calfskin. The experiments were usually made with half of a skin, the wet pickled weight being about 300 g. This was drummed in 6 liters of a 5-percent solution of sodium chloride for 24 hours. To this was added 120 g of ferric sulfate and the amounts of the organic acid indicated in table 1 for each 40 g of the ferric sulfate, except in the case of citric acid, where 9.6 g was used. Sufficient anhydrous sodium carbonate, usually about 50 g, was then added to bring the pH to approximately 2.5.

The drum was rotated for about 6 hours, and then the solutions were made more basic by the addition of sodium carbonate. The hide remained in the solution in the drum overnight, and the next day the solutions were brought to a pH of 3.75 to 4 by the addition of more sodium carbonate. After drumming for about 6 hours longer, the hide was washed thoroughly. It was then fat-liquored[3] with a mixture of sulfonated castor oil, sulfonated neat's-foot oil, and neat's-foot oil in the proportions of 15, 35, and 50 percent, respectively. The amount of fat liquor used was 5 percent of the wet pickled weight. The hide was then tacked on a board and dried. It was then removed from the board, sammied,[4] and staked.[5]

5. PROPERTIES OF THE LEATHERS

The leathers produced were light yellow to brown in color. The lightest colors were produced when gluconic and citric acids were used. On normal exposure to light the colors changed to deep brown. A sample dyed black with a direct dye (Pontamine black EX, Color Index 581) showed good fastness to light. The leathers were very flexible and seemed to be of good quality.

The chemical analyses, original tensile strengths, shrinkage temperatures, losses in tensile strength on aging, and pH of a water extract of the leather are shown in table 4. All the samples except No. 21, which was a calfskin, were goatskins. Eighty-five to ninety-nine percent of the ash was composed of Fe_2O_3. These percentages of ferric oxide are higher than the corresponding values for chromic oxide in well-tanned leather. The shrinkage temperatures of the iron-tanned leathers are low in comparison to those of chrome leathers. The calfskin leather gave the highest value for shrinkage temperature. However, this leather was thicker than the goatskin leathers, which may have had some influence on the result.

TABLE 4.—*Analysis of the iron-tanned leather and the results of the accelerated aging tests*

Hide number	Organic acid	Hide substance	Grease	Ash	Moisture	pH	Shrinkage temperature	Original tensile strength	Loss in tensile strength on aging
		%	%	%	%		°C	lb./in.²	%
1	Citric	59.9	5.9	11.7	11.7	3.3	80	1,850	20.5
2	Lactic	57.3	4.7	19.5	9.2	3.7	74	1,640	37.2
4	Citric	58.5	1.0	15.4	9.6	3.9	84	2,165	11.8
5	do	61.5	1.3	13.8	9.3	4.8	80	2,925	19.7
10	do	58.2	7.7	13.4	7.0	3.4	76	2,850	18.8
11	do	60.2	5.7	12.0	9.1	3.6	84	3,620	27.8
12	Hydroxyacetic	54.1	9.0	15.4	7.9	3.6	75	3,875	35.2
13	Citric	59.0	6.7	10.4	7.6	4.6	77	4,895	31.3
15[1]	do	47.7	21.3	10.1	7.1	4.5	80	4,425	31.2
19	Gluconic	55.7	11.6	14.5	10.4	3.6	------	2,905	50.1
20	do	55.5	12.7	7.6	10.7	3.4	77	3,695	54.4
21[2]	do	48.9	4.7	12.5	12.4	3.0	90	2,980	55.2

[1] Dyed black.
[2] Calfskins.

[3] Treated with an oil-water emulsion, from which oil is absorbed by the tanned hide.
[4] Treated to increase its moisture content by slow absorption from damp sawdust or from a similar material.
[5] Stretched by pulling it over the edge of a board or similar device.

The best iron-tanned leathers were exposed to accelerated aging conditions. Six control and six tensile-strength test specimens were cut from each sample of leather. Each control was cut adjacent to a test specimen. After the samples had been conditioned at 70° F and 65-percent relative humidity for 48 hours, they were placed in an exposure chamber maintained at 100°±2° C. Air saturated with moisture at 45° C was passed over the samples at a rate of 8 to 12 ml per minute. The air saturated at this temperature contained sufficient moisture to give a relative humidity of 9 to 11 percent in the chamber at 100° C.

The specimens were heated under these conditions for 7 days. They were then reconditioned at 70° F and 65-percent relative humidity and tested with the control samples which had remained in the conditioning room under the same conditions. The percentage loss in tensile strength of the aged samples was calculated from the difference between their average tensile strength and that of the control samples. The results are shown in table 4.

It is considered, from previous experience, that leather showing no more than a 20-percent loss in tensile strength has good resistance to aging; above 20 percent but no more than 35 percent is considered fair.

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WASHINGTON, September 3, 1943.

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[Continued on p. 4 of cover]

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Range of x	Interval between successive arguments
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7 to 50	01
50 to 300	.1
300 to 2.000	1
2,000 to 10,000	10

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